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SUMMARIES OF PAPERS PUBLISHED IN ANALYTICA CHIMICA ACTA

Vol. 26, No. 5, May 1962

SOME THEORETICAL CONSIDERATIONS IN ANALYTICAL CHEMISTRY

VI. THE PRECISE CALCULATION OF DATA FOR REDOX TITRATION CURVES

The dependence of the potentials during a redox titration upon the absolute concentrations of the reactants in the general case is demonstrated and an analogy is drawn between the effects of incompleteness of reaction in redox titrations and salt hydrolysis in acid–base reactions. The interpretation of the equilibrium constant of the overall redox reaction is clarified, and rigorous expressions for the calculation of reaction deficiencies are developed. Methods of calculating data for titration curves making allowance for reaction deficiency are offered together with examples of their application.

E. BISHOP, *Anal. Chim. Acta*, 26 (1962) 397–405

THE DETERMINATION OF CARBOXYL GROUPS IN POLYCAPROLACTAM

A new method for the determination of carboxyl groups in polycaprolactam is proposed. The polymer is dissolved in 2,6-xylenol and chloroform at 130°, and the carboxyl groups are titrated potentiometrically with ethanolic potassium hydroxide solution at 30°. The results are the same as those obtained by dissolution of the polymer in benzyl alcohol at 175° and titration at 135°, using phenolphthalein indicator. The advantage of the new method is that the titration is done nearly at room temperature, which is important in the analysis of coloured or pigmented polymers where the equivalence point must be indicated electrometrically.

M. J. MAURICE, *Anal. Chim. Acta*, 26 (1962) 406–409

GAS–LIQUID CHROMATOGRAPHIC ANALYSIS OF C_{10}–C_{16} *n*-PARAFFINS, ISOPARAFFINS AND α-OLEFINS IN A LOW-TEMPERATURE COAL TAR

21 C_{10}–C_{16} hydrocarbons, 7 each of *n*-paraffins, 2-methyl alkanes and α-olefins, were identified in a low-temperature bituminous coal tar by means of gas–liquid chromatography. Quantitative determinations were made on all of these constituents. It was found that the curves for the plots of logarithms of relative retention against normal boiling points for C_{10}–C_{16} *n*-paraffins and α-olefins are parallel. A similar parallel curve for the 2-methyl alkane series was derived, using the known point for 2-methyl decane. This correlation curve was used for the identification of several 2-methyl alkanes. Naphthenes and *trans*-olefins were found in small amounts.

T.-C. L. CHANG AND C. KARR, JR., *Anal. Chim. Acta*, 26 (1962) 410–418

CHROMATOGRAPHIC SEPARATION AND DETERMINATION OF FRUIT ACIDS

A method is described for the determination of malic, tartaric and citric acids and sugar in fruit juices. It consists of the separation of these constituents by ion-exchange chromatography through a column of Dowex 1-X8 with an acetate buffer as eluent, treatment of aliquots of the separated constituents with dichromate and sulfuric acid and measurement of the absorbance of the resultant green chromium(III).

A. J. GOUDIE AND W. RIEMAN III, *Anal. Chim. Acta*, 26 (1962) 419–423

SPOT TEST DETECTION OF TAURINE THROUGH DEMASKING AND PYROLYTIC EFFECTS

A test for taurine is described based on demasking of the inner-complex-bound sulfonic acid group by formaldehyde followed by pyrolysis reactions with mercury(II) cyanide or benzoin. The resulting hydrogen cyanide or sulfur dioxide can be detected in the gas phase by familiar color reactions. All the reactions may be conducted within the limits of spot test analysis. Microchemical limits of identification are attained.

F. FEIGL, *Anal. Chim. Acta*, 26 (1962) 424–426

MICROANALYSIS WITH THE AID OF ION-EXCHANGE RESINS

XIX. DETECTION OF NANOGRAM AMOUNTS OF IRON(III) WITH FERRON

A new ultramicro method for detection of iron(III) is described. A colourless, strongly basic anion-exchange resin of low cross-linkage in the chloride form is used to enhance the sensitivity of the colour reaction of iron(III) with ferron. The limit of identification of the new "resin spot test" is 4 ng of iron(III) ($1:1\cdot10^7$) after 10 to 20 min and 2 ng ($1:2\cdot10^7$) after 50 min. The test is 50–100 times as sensitive as the usual spot test. Serious interferences were observed with cobalt(II), copper(II), chromium(VI), uranium(VI) and vanadium(V); the elimination of their interferences was also studied.

M. FUJIMOTO AND Y. NAKATSUKASA, *Anal. Chim. Acta*, 26 (1962) 427–433

THE GRAVIMETRIC DETERMINATION OF ZIRCONIUM IN ZIRCONIUM CONCENTRATES

(in German)

A new gravimetric method involving tartrazine or flavazine L as reagent has been developed for the rapid determination of zirconium in zirconiferous concentrates. The methods are compared with the mandelic acid method and advantages are outlined.

GR. POPA, F. POPEA, D. CLUCERU AND GH. BAIULESCU, *Anal. Chim. Acta*, 26 (1962) 434–438

MECHANICAL FEED BURNER WITH TOTAL CONSUMPTION FOR FLAME PHOTOMETRY AND ATOMIC ABSORPTION SPECTROSCOPY

A mechanical feed burner has been developed for use in flame photometry and atomic absorption spectroscopy. The optimum flame conditions for emission and absorption are very different. These conditions are also modified when organic instead of aqueous solvents are used. When different organic solvents are used, the interference is eliminated with atomic absorption but not emission. Flame profiles of atomic absorption and emission signals indicate that the processes are independent; the best signal for each is obtained at different parts of the flame. With emission, it appears that line spectra and background emission originate from the same process *e.g.* chemiluminescence.

J. W. ROBINSON AND R. J. HARRIS, *Anal.Chim. Acta*, 26 (1962) 439–445

INFRARED STUDY OF THE COPPER–EDTA COMPLEX AND ITS REACTION WITH VARIOUS AMINO COMPOUNDS

Verification in the infrared region is provided for a recent visible range spectrophotometric study which suggested that ammonia and certain amino compounds enter the $[CuY]^{-2}$ complex and coordinate with the central copper in place of two carboxyl linkages. Such coordination occurs to a lesser extent with secondary than with primary amines, but almost not at all with tertiary amines, presumably because of steric factors. The freeze-drying method was used to obtain the $[CuY]^{-2}$ complex alone, or with coordinated amines, dispersed in solid potassium bromide which was pressed into disk-form for infrared analysis.

I. CITRON, *Anal. Chim. Acta*, 26 (1962) 446–457

A SPECTROPHOTOMETRIC STUDY OF *o,o'*-DIHYDROXYAZOBENZENE AND ITS CHELATES WITH ALUMINUM, GALLIUM AND INDIUM

The composition of the chelates of aluminum, gallium and indium with *o,o'*-dihydroxyazobenzene has been established in acidic alcoholic–water mixtures to be pH dependent by means of spectrophotometric measurements. Only chelates with a 1 : 1 and 2 : 1 ratio of *o,o'*-dihydroxyazobenzene to metal are formed. The first acid dissociation constant of *o,o'*-dihydroxyazobenzene and the formulas and stability constants for the chelates were determined. The stability of the chelates increased in the order indium, aluminum, gallium.

J. R. KIRBY, R. M. MILBURN AND J. H. SAYLOR, *Anal. Chim. Acta*, 26 (1962) 458–469

SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM AS VANADIUM(IV) PYRIDINE THIOCYANATE

A spectrophotometric determination of vanadium as vanadium(IV) pyridine thiocyanate is described. The blue complex is formed in acidic aqueous solution and extracted into pyridine–chloroform. Absorbance is measured at 740 mμ. The range of best accuracy for 1-cm cells is from about 80 to 240 μg of vanadium per ml, and the sensitivity is 0.4 μg of vanadium per cm^2 at 740 mμ. The vanadium may be present initially as vanadium(IV) or vanadium(V), which is reduced to vanadium(IV) by the large excess of thiocyanate ion added. Several elements interfere in the determination; a separation procedure involving mercury cathode electrolysis is suggested.

G. H. AYRES AND L. E. SCROGGIE, *Anal. Chim. Acta*, 26 (1962) 470–477

CHLORPROMAZINE HYDROCHLORIDE AS AN ANALYTICAL REAGENT

PART II. COLORIMETRIC DETERMINATION OF MICRO QUANTITIES OF GOLD

Chlorpromazine hydrochloride is proposed for the colorimetric determination of gold in acidic medium at 530 mμ. Comparatively large amounts of copper, silver, iron, lead, etc. can be tolerated. The colour is stable; Beer's law is obeyed over the range 0.5–8 μg of gold per ml.

LEE KUM-TATT, *Anal. Chim. Acta*, 26 (1962) 478–481

SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM WITH 1,2-DIAMINOCYCLOHEXANETETRAACETIC ACID

Chromium(III) forms a water-soluble complex with DCTA. The violet complex has maximum absorbance at 540 mμ and obeys Beer's law from 2 to 150 μg chromium per ml. The molar extinction coefficient is 245. Determinations of copper and chromium, cobalt and chromium, and nickel and chromium in presence of each other are described. The complex contains chromium and the reagent in a ratio of 1 : 1. The stability constant of the complex is $1.9 \cdot 10^{22}$.

A. R. SELMER-OLSEN, *Anal. Chim. Acta.*, 26 (1962) 482–486

THE REACTION OF THORIUM WITH 1-(1-HYDROXY-4-METHYL-2-PHENYLAZO)-2-NAPHTHOL-4-SULFONIC ACID IN PRESENCE OF EDTA AND ITS APPLICATION IN THE SPECTROPHOTOMETRIC DETERMINATION OF THORIUM IN URINE

1-(1-Hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid (Calmagite) can be used for the spectrophotometric determination of thorium in urine, by employing EDTA and hydroxylamine as masking agents. By the method of continuous variations, it was found that two moles of Calmagite reacted with one mole of thorium, and that the apparent stability constant was $2.4 \cdot 10^8$ at pH 8.5. A procedure was developed for the rapid wet oxidation of urine, using a mixture of nitric, perchloric and sulfuric acids. The sensitivity of the reaction for thorium was found to be 0.008 μg per square cm per 0.001 absorption unit at 640 mμ. The molar absorptivity of the thorium complex was found to be 53000 at 640 mμ at pH 10.0.

P. J. CURCIO AND P. F. LOTT, *Anal. Chim. Acta*, 26 (1962) 487–494

A SPECTROPHOTOMETRIC ASSAY OF WATER IN ORGANIC SOLVENTS

(Short Communication)

R. C. R. BARRETO AND H. S. R. BARRETO, *Anal. Chim. Acta*, 26 (1962) 494–495

A MODIFIED ISOPIESTIC METHOD FOR THE MICRO-DETERMINATION OF MOLECULAR WEIGHTS

(Short Communication)

R. S. BORAMAN AND A. D. CAMPBELL, *Anal. Chim. Acta*, 26 (1962) 496–498

A SENSITIVE TEST FOR NITRATE

(Short Communication)

G. DE VRIES AND A. A. A. M. BRINKMAN, *Anal. Chim. Acta*, 26 (1962) 498–500

SOME THEORETICAL CONSIDERATIONS IN ANALYTICAL CHEMISTRY

PART VI*. THE PRECISE CALCULATION OF DATA FOR REDOX TITRATION CURVES

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(Received August 15th, 1961)

In the simple calculation of redox potentials for titration curves[1] from the Nernst equation and reactant concentrations, the potentials are a logarithmic function of the ratio of the concentrations of the active species and appear to be independent of absolute concentration. This also applies to the equilibrium constant of the overall titrimetric reaction[2] and, when the reaction coefficients are homogeneous, to certain other quantitative factors[2], but does not apply when the reaction coefficients are inhomogeneous[2,3]. In the latter circumstance, such factors as the equivalence point potential[3] and the quantitativeness of the reaction[2] become dependent on the absolute concentrations of the reactants. As will be shown, in even the simplest reactions having unit coefficients and involving the transfer of a single electron, the calculation of the potentials becomes concentration-dependent when any attempt is made to take account of incompleteness of reaction. The effect of such reaction deficiency is to flatten the horizontal part of the curve and to decrease the rate of change of potential through the equivalence point. This enhanced potentiostatic buffering is similar to the effect of hydrolysis of salts in acid–base titrations. The analogy with buffer solutions and titrations involving such media[1,4,5] extends to the situation that whereas the simple calculation employs concentration ratios, precise calculation invokes absolute concentrations, and reveals that buffering is more efficient than the simple calculation predicts[5]. The extent of this potentiostasis may be judged from the example of a customary titration with a difference in normal potential of oxidant and reductant of 0.2 V and the transfer of a single electron, wherein at 0.1% from the equivalence point the alteration in potential due to incompleteness of reaction is no less than 81 mV. For a reaction involving the transfer of two electrons and having a difference in normal potential of 0.4 V, the corresponding effect of incompleteness of reaction is diminished to 0.6 mV. The effect of increasing difference in normal potential in redox titrations finds an analogy in the effect of increasing ionisation constant in acid–base titrations, so that reaction deficiency corresponds to solvolysis. Analogies can also be discovered with other types of ion combination reactions.

The usual procedure in the preparation of a redox curve[1] is to calculate the poten-

* Part V see *Anal. Chim. Acta*, 22 (1960) 205.

tial of the reductant system prior to the equivalence point and the potential of the oxidant system after the equivalence point, and to combine the two half curves with the equivalence point potential. The effect of neglecting the incompleteness of reaction is immediately revealed in examples such as the one first mentioned (*cf.* Fig. 1). The two halves of the curve refuse to mate, although a continuous curve can be recorded experimentally and the interval between the normal potentials is generally considered acceptable.

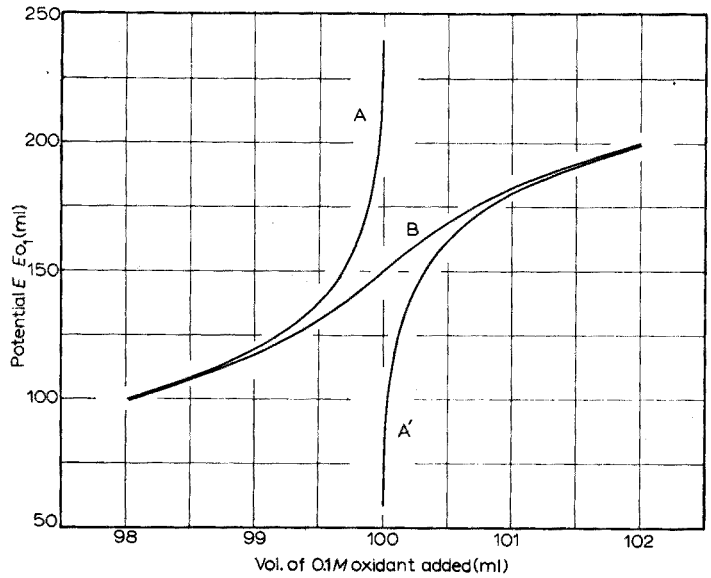

Fig. 1. Titration of 100 ml of 0.1 *M* reductant with 0.1 *M* oxidant at 30°. $\Delta E_0 = 0.3$ V; $a = b = c = d = n_1 = n_2 = 1$. A, A', calculated by the simple method directly from apparent concentrations and the Nernst equation. B, calculated by the described method.

No account of this situation, other than at the equivalence point[1,6], appears to be recorded in the standard texts. It has proved possible to evolve a mathematical treatment for the completely general case, and methods of calculating the reaction deficiencies and the points for titration curves are presented here. Some observations on the consequences of the incompleteness of redox reactions will be offered in a subsequent Part.

Equilibrium constant

The incompleteness of reaction at any selected stage in the titration can be derived from the equilibrium constant, which in turn can be derived from the normal potentials of the reactants. The apparent concentrations of the reactants can then be corrected for reaction deficiency and the true values used in the appropriate Nernst equation to calculate the potential at the selected stage in the titration. It is first necessary to clarify the interpretation of n, the number of electrons transferred, which appears in the expression for the equilibrium constant[2].

Let the oxidant system, of normal potential E_{0_1}, be represented by eqn. (1), and the reductant system, of normal potential E_{0_2}, be represented by eqn. (2). Multiplica-

tion of eqn. (1) by x and of eqn. (2) by y where $n_1x = n_2y$, followed by addition gives the balanced eqn. (3) for the overall titrimetric reaction.

$$a\mathrm{Ox}_1 + n_1\varepsilon \rightleftharpoons c\mathrm{Red}_1 \quad (1)$$

$$b\mathrm{Red}_2 \rightleftharpoons n_2\varepsilon + d\mathrm{Ox}_2 \quad (2)$$

$$ax\mathrm{Ox}_1 + by\mathrm{Red}_2 \rightleftharpoons cx\mathrm{Red}_1 + dy\mathrm{Ox}_2 \quad (3)$$

The equilibrium constant for the overall reaction is then

$$\frac{[\mathrm{Red}_1]^{cx}[\mathrm{Ox}_2]^{dy}}{[\mathrm{Ox}_1]^{ax}[\mathrm{Red}_2]^{by}} = K \quad (4)$$

At any selected point in the titration, when the reaction has reached equilibrium, the potentials of the two systems E will be the same.

$$E = E_{0_1} + \frac{0.0002T}{n_1}\log\frac{[\mathrm{Ox}_1]^a}{[\mathrm{Red}_1]^c} = E_{0_2} + \frac{0.0002T}{n_2}\log\frac{[\mathrm{Ox}_2]^d}{[\mathrm{Red}_2]^b}$$

$$= E_{0_1} - \frac{0.0002T}{n_1x}\log\frac{[\mathrm{Red}_1]^{cx}}{[\mathrm{Ox}_1]^{ax}} = E_{0_2} + \frac{0.0002T}{n_2y}\log\frac{[\mathrm{Ox}_2]^{dy}}{[\mathrm{Red}_2]^{by}}$$

Since $n_1x = n_2y$, and writing $E_{0_1} - E_{0_2} = \Delta E_0$,

$$\frac{xn_1\Delta E_0}{0.0002T} = \frac{yn_2\Delta E_0}{0.0002T} = \log\frac{[\mathrm{Red}_1]^{cx}[\mathrm{Ox}_2]^{dy}}{[\mathrm{Ox}_1]^{ax}[\mathrm{Red}_2]^{by}} = \log K \quad (5)$$

The number of electrons in the expression for the equilibrium constant is therefore the least common multiple of the number of electrons transferred in each of the two half reactions.

Reaction deficiency

In the simple calculation of curve data assuming the reaction to be complete, the ratio of [Ox] to [Red] is alone required, and is derived from the fraction of the equivalence volume of titrant added before the equivalence point, and thereafter from the excess of titrant: concentrations and dilution factors cancel out. Concentrations, when needed, can be calculated from the initial concentration and volume of titrand, the initial concentration and volume of titrant and the overall reaction stoichiometry. Let the apparent concentrations so calculated be C_{ox_1}, C_{red_1}, C_{ox_2} and C_{red_2} at any selected point in the titration. These concentrations are inter-related through the reaction coefficients of eqn. (3).

Before the equivalence point, with the oxidant as titrant, let the reaction deficiency be denoted by the amount of Red_2, expressed as a concentration δ_{red_2}, which has failed to react with Ox_1 due to incompleteness of reaction. Then,

$$[\mathrm{Ox}_2] = C_{\mathrm{ox}_2} - \frac{d}{b}\delta_{\mathrm{red}_2} \quad (6)$$

$$[\mathrm{Red}_2] = C_{\mathrm{red}_2} + \delta_{\mathrm{red}_2} \quad (7)$$

$$[\mathrm{Ox}_1] = \frac{ax}{by}\delta_{\mathrm{red}_2} \quad (8)$$

$$[\mathrm{Red}_1] = C_{\mathrm{red}_1} - \frac{cx}{by}\delta_{\mathrm{red}_2} = \frac{cx}{dy}C_{\mathrm{ox}_2} - \frac{cx}{by}\delta_{\mathrm{red}_2} \quad (9)$$

Substitution in (5) in terms of the reductant system gives

$$\frac{yn_2\Delta E_0}{0.0002T} = \log \frac{\left(\frac{cx}{dy}C_{ox_2} - \frac{cx}{by}\delta_{red_2}\right)^{cx}\left(C_{ox_2} - \frac{d}{b}\delta_{red_2}\right)^{dy}}{\left(\frac{ax}{by}\delta_{red_2}\right)^{ax}\left(C_{red_2} + \delta_{red_2}\right)^{by}} \tag{10}$$

From the relationship $n_1x = n_2y$, (10) becomes, in terms of n_1 and n_2,

$$\frac{n_1n_2\Delta E_0}{0.0002T} = \log \frac{\left(\frac{cn_2}{dn_1}C_{ox_2} - \frac{cn_2}{bn_1}\delta_{red_2}\right)^{cn_2}\left(C_{ox_2} - \frac{d}{b}\delta_{red_2}\right)^{dn_1}}{\left(\frac{an_2}{bn_1}\delta_{red_2}\right)^{an_2}\left(C_{red_2} + \delta_{red_2}\right)^{bn_1}} \tag{11}$$

Since eqn. (10) involves the L.C.M. of n_1 and n_2, it may be of a lower order and therefore more readily soluble than eqn. (11).

It is seldom necessary to invoke the completely general case covered by the preceding equations. Very commonly, $a = b = c = d = 1$, but $n_1 \neq n_2$ (*i.e.* $x \neq y$), when eqn. (10) simplifies to

$$\frac{yn_2\Delta E_0}{0.0002T} = \log \frac{(C_{ox_2} - \delta_{red_2})^{(x+y)}}{(\delta_{red_2})^x(C_{red_2} + \delta_{red_2})^y} \tag{12}$$

and eqn. (11) simplifies to

$$\frac{n_1n_2\Delta E_0}{0.0002T} = \log \frac{(C_{ox_2} - \delta_{red_2})^{(n_1+n_2)}}{(\delta_{red_2})^{n_2}(C_{red_2} + \delta_{red_2})^{n_1}} \tag{13}$$

Eqn. (12) may again be of a lower order than eqn. (13). Application of the assumption that δ_{red_2} becomes negligible with respect to C_{ox_2} close to the equivalence point does not reduce the order of the equation, and it is only when the approach to equivalence is so close that C_{red_2} becomes negligible with respect to δ_{red_2} that the order diminishes and the equation collapses to first order, a situation which does not fall to be examined in practice.

For symmetrical reactions where $n_1 = n_2$, which are not uncommon, the equations resolve into a simple quadratic which is susceptible of formula solution:

$$\frac{n_2\Delta E_0}{0.0002T} = \log \frac{(C_{ox_2} - \delta_{red_2})^2}{\delta_{red_2}(C_{red_2} + \delta_{red_2})} \tag{14}$$

Setting the antilog of the quantity on the left hand side equal to A, (14) yields,

$$(A-1)\delta_{red_2}{}^2 + (AC_{red_2} + 2C_{ox_2})\delta_{red_2} - C_{ox_2}{}^2 = 0 \tag{15}$$

Following the equivalence point, again with the oxidant as titrant, let the reaction deficiency be denoted by the amount of Ox_1 expressed as a concentration δ_{ox_1}, which

has failed to react with Red_2, due to incompleteness of reaction. Then, using the coefficients of reaction (3),

$$[Ox_1] = C_{ox_1} + \delta_{ox_1} \tag{16}$$

$$[Red_1] = C_{red_1} - \frac{c}{a}\delta_{ox_1} \tag{17}$$

$$[Red_2] = \frac{by}{ax}\delta_{ox_1} \tag{18}$$

$$[Ox_2] = C_{ox_2} - \frac{dy}{ax}\delta_{ox_1} = \frac{dy}{cx}C_{red_1} - \frac{dy}{ax}\delta_{ox_1} \tag{19}$$

Substitution in (5) in terms of the oxidant system gives

$$\frac{xn_1\Delta E_0}{0.0002T} = \log \frac{\left(C_{red_1} - \frac{c}{a}\delta_{ox_1}\right)^{cx}\left(\frac{dy}{cx}C_{red_1} - \frac{dy}{ax}\delta_{ox_1}\right)^{dy}}{\left(C_{ox_1} + \delta_{ox_1}\right)^{ax}\left(\frac{by}{ax}\delta_{ox_1}\right)^{by}} \tag{20}$$

From the relationship $n_1x = n_2y$, (20) becomes, in terms of n_1, n_2

$$\frac{n_1n_2\Delta E_0}{0.0002T} = \log \frac{\left(C_{red_1} - \frac{c}{a}\delta_{ox_1}\right)^{cn_2}\left(\frac{dn_1}{cn_2}C_{red_1} - \frac{dn_1}{an_2}\delta_{ox_1}\right)^{dn_1}}{\left(C_{ox_1} + \delta_{ox_1}\right)^{an_2}\left(\frac{bn_1}{an_2}\delta_{ox_1}\right)^{bn_1}} \tag{21}$$

Once again in the more common case where $a = b = c = d = 1$, but $n_1 \neq n_2$, eqn. (20) simplifies to

$$\frac{xn_1\Delta E_0}{0.0002T} = \log \frac{(C_{red_1} - \delta_{ox_1})^{(x+y)}}{(\delta_{ox_1})^y(C_{ox_1} + \delta_{ox_1})^x} \tag{22}$$

and eqn. (21) simplifies to

$$\frac{n_1n_2\Delta E_0}{0.0002T} = \log \frac{(C_{red_1} - \delta_{ox_1})^{(n_1+n_2)}}{(\delta_{ox_1})^{n_1}(C_{ox_1} + \delta_{ox_1})^{n_2}} \tag{23}$$

Finally, for symmetrical reactions where $n_1 = n_2$, both (20) and (21) resolve into the quadratic (24), A having the same meaning as before

$$(A - 1)\delta_{ox_1}^2 + (AC_{ox_1} + 2C_{red_1})\delta_{ox_1} - C_{red_1}^2 = 0 \tag{24}$$

Solution of the equations. Eqns. (15) and (24) for symmetrical reactions are simply and easily soluble by manual methods. For totally unsymmetrical reactions, however, eqns. (11) and (21) may run up to the 16th order, though by using the form of (10) and (20) an equation of the 8th order results. Even reactions with homogeneous coefficients may run eqns. (12), (13), (22) and (23) up to the 7th order. With the aid of the physical meaning of the quantities involved, manual solution is still possible by the method of successive approximations, but the operations are lengthy and tedious and a poor first guess occasions many circuits of the loop. The equations can be

programmed quite easily for computational analysis and solution by digital computer is both possible and fast.

Calculation of curve data

Since the desired plot is of potential *versus* titrant volume, the basic variables are titrant volume and reaction deficiency. These may be incorporated in one or more comprehensive equations, but the equations then become cumbersome and cause repetitional operations. It is therefore more convenient to use sequential operations, as follows.

(*i*) Calculate A from supplied values of n and ΔE_0.

(*ii*) Calculate C_{ox_2} and C_{red_2} (before equivalence) or C_{ox_1} and C_{red_1} (after equivalence) for the selected value of the titrant volume (*vide infra*).

(*iii*) Calculate δ_{red_2} (before equivalence) or δ_{ox_1} (after equivalence) from the appropriate equations above, and the data of (*i*) and (*ii*).

(*iv*) Calculate the true concentrations as required from eqns. (6)–(9) or (16)–(19).

(*v*) Substitute the concentrations from (*iv*) in the appropriate Nernst equation and calculate E.

In operation (*ii*) let the molarity of the titrant (oxidant) be M_O, the molarity of the titrand (reductant) be M_R and the initial volume of the titrand be v_R ml. Before the equivalence point, from the stoichiometry of reaction (3), after the addition of v ml of titrant, the apparent concentrations are given, in the alternative forms, by

$$C_{red_1} = \frac{C v M_O}{a(v + v_R)} \tag{25}$$

$$C_{red_2} = \frac{ax v_R M_R - by v M_O}{ax(v + v_R)} = \frac{an_2 v_R M_R - bn_1 v M_O}{an_2(v + v_R)} \tag{26}$$

$$C_{ox_2} = \frac{dy v M_O}{ax(v + v_R)} = \frac{dn_1 v M_O}{an_2(v + v_R)} \tag{27}$$

After the equivalence point, greater precision is more readily accessible by working in terms of the volume v' of the titrant added in excess of the equivalence volume. The equivalence volume of titrant is

$$v = \frac{ax M_R}{by M_O} v_R = \frac{an_2 M_R}{bn_1 M_O} v_R \tag{28}$$

The total volume V of the titration solution at the equivalence point is then

$$V = \left(\frac{ax M_R}{by M_O} + 1\right) v_R = \left(\frac{an_2 M_R}{bn_1 M_O} + 1\right) v_R \tag{29}$$

and the apparent concentrations in terms of v' and V are

$$C_{ox_1} = \frac{v' M_O}{(V + v')} \tag{30}$$

$$C_{red_1} = \frac{cx M_R v_R}{by(V + v')} = \frac{cn_2 M_R v_R}{bn_1(V + v')} \tag{31}$$

$$C_{ox_2} = \frac{d M_R v_R}{b(V + v')} \tag{32}$$

Eqns. (25) to (32) simplify in an obvious way when the reaction coefficients are homogeneous and further when the reaction is symmetrical. Apart from the enhanced precision gained by the use of v' there is no need to change from one system to the other on passing the equivalence point.

RESULTS

The method may be illustrated by the example of a symmetrical monoelectronic reaction, where $a = b = c = d = n_1 = n_2 = 1$, in the titration of 100 ml of 0.1 M reductant with 0.1 M oxidant. The significant results are presented in tabular form (Table I) for a reaction in which the difference in normal potential between oxidant and reductant, ΔE_0, is 0.2 V; the final column shows the value of the error in potential δE arising from neglecting the incompleteness of reaction. The titration curve calculated for a reaction in which ΔE_0 is 0.3 V is given in Fig. 1, together with the two half curves calculated without allowing for incompleteness of reaction. The proposed method gives a smooth curve passing accurately through the correct equivalence point potential, whereas the simple method gives two non-mating curves with a large gap in the middle despite the fairly high value of ΔE_0.

TABLE I

TITRATION OF 100 ml OF 0.1 M REDUCTANT WITH 0.1 M OXIDANT AT 30° FOR A REACTION FOR WHICH $a = b = c = d = n_1 = n_2 = 1$ AND $\Delta E_0 = 200$ mV

Volume of titrant added v ml	δ *M*	*Potential* $E - E_{0_2}$ *mV*	*Approximate potential* $E - E_{0_2}$ *mV*	*Error in potential due to neglect of* δ_{red_2} δE *mV*
	δ_{red_2}			
98	$6.61 \cdot 10^{-4}$	88	101.4	13.4
99	$8.31 \cdot 10^{-4}$	93.75	120	26.2
99.5	$9.34 \cdot 10^{-4}$	97	138	41
99.8	$1.002 \cdot 10^{-3}$	98	162	64
99.9	$1.03 \cdot 10^{-3}$	99	180	81
99.98	$1.049 \cdot 10^{-3}$	99.5	222	122
99.99	$1.051 \cdot 10^{-3}$	100	240	140
100	$1.053 \cdot 10^{-3}$	100	—	
	δ_{ox_2}			
100.01	$1.051 \cdot 10^{-3}$	100	−40	140
100.02	$1.049 \cdot 10^{-3}$	100.5	−22	122
100.1	$1.031 \cdot 10^{-3}$	101	+20	81
100.2	$1.005 \cdot 10^{-3}$	102	+38	64
100.5	$9.38 \cdot 10^{-4}$	103	+62	41
101	$8.34 \cdot 10^{-4}$	106.1	+80	26.1
102	$6.66 \cdot 10^{-4}$	111.9	+98	13.9

It may be noted that in the simple method the calculation before equivalence based on the reductant system is entirely unconnected with the calculation after equivalence based on the oxidant system, and a separate calculation is required for the equivalence point potential. In the proposed method, the whole series of calculations, including that of the equivalence point potential, can be made on either reductant or oxidant system: there is no need to change over on passing the equivalence point.

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APPENDIX

Example of the method of calculation for symmetrical reactions

For instance, let $n_1 = n_2 = 2$; $a = b = c = d = 1$; $\Delta E_0 = 0.2$ V; temperature 30°, $M_O = M_R = 5 \cdot 10^{-2} M$.

(*i*) $A =$ antilog $(2 \cdot 0.2/0.06) =$ antilog $6.667 = 4.645 \cdot 10^6$. (This is the equilibrium constant for the reaction).

(*ii*) After adding 99.9 ml (v) of oxidant to 100 ml (v_R) of reductant, from eqns. (26) and (27), $C_{red_2} = 2.501 \cdot 10^{-5}$ and $C_{ox_2} = 2.499 \cdot 10^{-2}$.

(*iii*) From eqn. (15) the reaction deficiency is given by

$$\delta_{red_2} = \frac{1}{2(A-1)} \{[(AC_{red_2} + 2C_{ox_2})^2 + 4(A-1)C_{ox_2}{}^2]^{\frac{1}{2}} - (AC_{red_2} + 2C_{ox_2})\} \qquad (33)$$

Substitution of the values of A, C_{red_2} and C_{ox_2} from (*i*) and (*ii*) and solution of (33) gives $\delta_{red_2} = 4.56 \cdot 10^{-6}$.

(*iv*) From eqns. (6) and (7), $[Ox_2] = 2.499 \cdot 10^{-2} - 4.56 \cdot 10^{-6} = 2.499 \cdot 10^{-2}$; $[Red_2] = 2.501 \cdot 10^{-5} + 4.56 \cdot 10^{-6} = 2.951 \cdot 10^{-5}$.

(*v*) $$E_2 = E_{0_2} + \frac{0.06}{2} \log \frac{2.499 \cdot 10^{-2}}{2.957 \cdot 10^{-5}} = E_{0_2} + 0.0878 \text{ V}.$$

Example of the method of successive approximations for step (iii) for homogeneous and inhomogeneous reactions

For instance, let $n_1 = 3$, $n_2 = 2$; $x = 2$, $y = 3$; $a = b = c = d = 1$; temperature 30°; $\Delta E_0 = 0.1$ V; $M_O = 3.33 \cdot 10^{-2}$, $M_R = 5 \cdot 10^{-2}$.

From step (*i*), $A = 10^{10}$. After adding 99.9 ml of oxidant to 100 ml of reductant, $C_{red_2} = 2.5 \cdot 10^{-5}$, $C_{ox_2} = 2.5 \cdot 10^{-2}$.

(*iii*) From eqn. (12),

$$10^{10} = \frac{(2.5 \cdot 10^{-2} - \delta_{red_2})^5}{\delta_{red_2}{}^2 (2.5 \cdot 10^{-5} + \delta_{red_2})^3}$$

or

$$\frac{(2.5 \cdot 10^{-2} - \delta_{red_2})^5}{\delta_{red_2}{}^2 (2.5 \cdot 10^{-5} + \delta_{red_2})^3 \cdot 10^{10}} = 1 \qquad (34)$$

Inspection quickly shows that to remove the powers of 10, δ_{red_2} is of the order of 10^{-4}. Try $2 \cdot 10^{-4}$.

$$\frac{2.485 \cdot 10^{-10}}{4 \cdot 10^{-8} \cdot 2.25^3 \cdot 10^{-12} \cdot 10^{10}} > 1$$

A trial at $2.5 \cdot 10^{-4}$ gives a value of less than 1.

At $2.3 \cdot 10^{-4}$, $2.477^5 \cdot 10^{-10}/2.3^2 \cdot 2.55^3 \cdot 10^{-10} = 1.06$. At $2.35 \cdot 10^{-4}$, $2.4765^5/2.35^2 \cdot 2.6^3 = 0.96$. So $\delta_{red_2} = 2.33 \cdot 10^{-4}$.

(*iv*) $[Ox_2] = 2.5 \cdot 10^{-2} - 2.33 \cdot 10^{-4} = 2.48 \cdot 10^{-2}$; $[Red_2] = 2.5 \cdot 10^{-5} + 2.33 \cdot 10^{-4} = 2.58 \cdot 10^{-4}$.

(*v*) $$E_2 = E_{0_2} + \frac{0.06}{2} \log \frac{2.48 \cdot 10^{-2}}{2.58 \cdot 10^{-4}} = E_{0_2} + 0.0305 \text{ V}.$$

SUMMARY

The dependence of the potentials during a redox titration upon the absolute concentrations of the reactants in the general case is demonstrated and an analogy is drawn between the effects of incompleteness of reaction in redox titrations and salt hydrolysis in acid–base reactions. The interpretation of the equilibrium constant of the overall redox reaction is clarified, and rigorous expressions for the calculation of reaction deficiencies are developed. Methods of calculating data for titration curves making allowance for reaction deficiency are offered together with examples of their application.

RÉSUMÉ

L'auteur a effectué une étude théorique sur la relation entre les potentiels et les concentrations des réactifs, au cours d'un titrage rédox, montrant l'analogie entre les effets d'une réaction incomplète lors de titrages redox et l'hydrolyse dans les réactions acide–base. Des méthodes de calculs de courbes de titrage sont proposées et des exemples sont donnés.

ZUSAMMENFASSUNG

Es wird die Abhängigkeit der Potentiale bei Redox-Titrationen von der Konzentration der Reagenzien nachgewiesen und auf die Analogie zwischen unvollständiger Reaktion bei Redox-Titrationen und Hydrolyse bei Säure–Basen Reaktionen hingewiesen. Der Verlauf der Titrationskurven wird mathematisch behandelt.

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THE DETERMINATION OF CARBOXYL GROUPS IN POLYCAPROLACTAM

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INTRODUCTION

In connection with such problems as the equivalence of terminal groups in polycaprolactam[1] it is of interest to determine both amino and carboxyl groups. The amino groups can be determined easily by dissolving the polymer at room temperature in a mixture of phenol and ethylene glycol and subsequent titration with hydrochloric acid in the same solvent, using thymol blue as an indicator[2].

As far as we know, the literature mentions only one solvent for determining carboxyl groups in this polymer. According to WALTZ AND TAYLOR[3] these groups can be determined by dissolution of the polymer in benzyl alcohol at 175° and titration with 0.1 *N* potassium hydroxide in a mixture of methanol and benzyl alcohol (1:9), using phenolphthalein as an indicator. According to HERMANS[4], who investigated polymers with an average molecular weight under 10,000, these groups can be determined by dissolution in the same solvent at 130°, followed by cooling to 60° and potentiometric titration with aqueous potassium hydroxide solution. WANG and co-workers[1] follow practically the same procedure, but titrate at room temperature with ethanolic sodium hydroxide solution, using a mixed indicator of phenolphthalein and thymol blue.

In our experience technical polymers with an average molecular weight of about 20,000 cannot be readily dissolved in benzyl alcohol at 130°. A much higher dissolution temperature is desirable. The lowest temperature at which the titration can be carried out is about 130°.

When coloured or pigmented polymers are to be analyzed, electrometric indication of the equivalence point of the titration is necessary. In this case, titration at a much lower temperature is preferable. Moreover, the use of benzyl alcohol as a solvent has the disadvantage that during dissolution at 175° an amount of acid is formed[3]. In order to avoid this oxidation of the solvent, oxygen must be rigorously excluded during dissolution[4].

In view of these facts it was decided to seek a solvent in which the polymer can be dissolved and titrated at a much lower temperature, preferably at room temperature.

EXPERIMENTAL

It will be understood that for this determination a protophilic solvent is to be preferred. However, the polymer cannot be dissolved in solvents such as pyridine,

dimethylformamide, aniline, benzylamine and ethylenediamine. Nor are amphiprotic and neutral solvents (butanol, ethylene glycol and tetrachloroethane) capable of dissolving the polymer. In a protogenic solvent such as a mixture of phenol and chloroform, the polymer can be dissolved quickly, but a titration of the carboxyl groups is impossible in this medium. Thus, it was necessary to find a solvent with less protogenic properties. It was found that when this protogenic character decreases, the solubility of the polymer decreases as well: the polymer can be dissolved in a mixture of phenol and chloroform (1:9) and in a mixture of *o*-cresol and chloroform (2:3), but not in a mixture of *o*-cresol and chloroform (1:9). Dissolution in *o*-cresol and chloroform (2:3) takes much longer than dissolution in phenol and chloroform (1:9). It was found that in a mixture of *o*-cresol and chloroform (2:3) the titration could not be performed, however.

Next, a mixture of 2,6-xylenol and chloroform was tried. In this solvent the carboxyl groups could be titrated potentiometrically with 0.1 *N* ethanolic potassium hydroxide solution: the difference in potential around the equivalence point was about 90 mV per 0.1 ml of titrant added.

In this case 2 g of polymer was dissolved in a mixture of 40 g of 2,6-xylenol and 10 g of chloroform by heating under reflux at 130°. Within 30 min this amount of polymer had dissolved quantitatively. After cooling to about 30° the solution remained clear. After each addition of ethanolic potassium hydroxide solution during the titration it took some time for the potential to become stable. This disadvantage could be overcome by adding 2 ml of acetone to the solution after dissolution of the polymer.

TABLE I

CARBOXYL CONTENT OF POLYCAPROLACTAM IN MEQUIV./113 g

Operator	*Sample*	*Visual determination in benzyl alcohol acc. to Waltz and Taylor, x*	*Potentiometric determination in 2,6-xylenol–chloroform–acetone acc. to our method, y*	*Difference* $d = \bar{x} - \bar{y}$
A	1	5.48	5.54	
		5.48	5.59	−0.08
		5.48	5.54	
	2	7.18	7.11	
		7.18	7.12	−0.02
		7.06	7.24	
	3	6.10	6.05	
		6.05	5.98	+0.05
		6.10	6.05	
B	4	7.37	7.29	
		7.41	7.23	+0.12
		7.36	7.26	
	5	4.99	4.99	
		4.91	5.06	−0.06
		4.97	5.01	
	6	5.33	5.41	
		5.31	5.49	−0.12
		5.35	5.46	
	7	7.55	7.34	
		7.58	7.35	+0.17
		7.56	7.48	
Mean				$\bar{d} = +0.01$
Standard deviation		$s_x = 0.031$	$s_y = 0.051$	$s_d = 0.11$

It should be noted that it is not always necessary to carry out a blank determination. A rigorous purification of the solvent chemicals is then a prerequisite.

On the basis of these results a procedure was developed, which is given in detail at the end of this paper. According to this procedure three samples of polycaprolactam were analyzed in triplicate for carboxyl groups. In these titrations a model H2-Beckman pH-meter with an S.C.E. and a glass electrode was used. The samples were also analyzed according to the method of WALTZ AND TAYLOR[3], the solution being cooled to 135° before titration (see Table I, A 1, 2, 3). Next, four other samples were analyzed in triplicate according to both methods, by an operator who had not taken part in the preliminary experiments of this investigation and therefore had no experience of the method developed (see Table I, B 4, 5, 6, 7). All seven samples contained acetic acid as a stabilizer. The results obtained are listed in Table I.

DISCUSSION

No systematic differences between the results of the two methods, given in Table I, can be detected by the *t*-test, so that it may be concluded that both methods give the same results. The standard deviations of single determinations do not differ significantly between operators for each method. These standard deviations were, therefore, combined and the overall values found are given in Table I. With the *F*-test no difference can be detected between the two reported standard deviations on the 0.05-level, so that the methods must be assumed to be of equal precision. This precision must be considered satisfactory.

It should be remarked that the aim of this investigation, *viz.* to find a solvent in which the polymer can be dissolved at room temperature, was not reached. However, the dissolution temperature is much lower for the proposed solvent than for benzyl alcohol and the titration can be carried out at nearly room temperature, which is of special importance in the case of coloured or pigmented polymers which must be analyzed electrometrically.

In addition to the experiments with potentiometric titrations, efforts were made to carry out the titration with HF-indication of the end-point. These efforts did not meet with any success, which is probably due to the low conductivity of the solution. The conductivity could not be increased by addition of an extra amount of acetone, because in that case the polymer would precipitate.

RECOMMENDED PROCEDURE

Reagents

(*a*) 2,6-xylenol, c.p. (British Drug Houses), purified by distillation.

(*b*) chloroform, c.p., purified by shaking with sodium carbonate solution, drying over anhydrous sodium sulphate, and distillation.

(*c*) acetone, c.p.

(*d*) ethanolic potassium hydroxide solution, 0.1 (*t*) *N*.

Procedure

Weigh out in a 200-ml beaker about 2 (*p*) g of ground polycaprolactam to the nearest 0.005 g. Add 40 g of 2,6-xylenol and 10 g of chloroform. Fit the beaker with a condenser via an adapter. Heat to boiling on a hot plate and boil until the sample has dissolved. This takes 30 min at most. Add by pipette 2 ml of acetone through the

condenser and swirl. Cool to about 30° and add 10 ml of chloroform dropwise by pipette whilst swirling constantly. Immerse a glass electrode and an S.C.E. in the solution, stir and titrate potentiometrically with t N ethanolic potassium hydroxide solution, using a microburette (v_1 ml). Carry out a blank by titrating the solvent with this titrant (v_0 ml). The sample contains:

$$\frac{113\,(v_1 - v_0)t}{p} \text{ mequiv. COOH/113 g.}$$

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SUMMARY

A new method for the determination of carboxyl groups in polycaprolactam is proposed. The polymer is dissolved in 2,6-xylenol and chloroform at 130°, and the carboxyl groups are titrated potentiometrically with ethanolic potassium hydroxide solution at 30°. The results are the same as those obtained by dissolution of the polymer in benzyl alcohol at 175° and titration at 135°, using phenolphthalein indicator. The advantage of the new method is that the titration is done nearly at room temperature, which is important in the analysis of coloured or pigmented polymers where the equivalence point must be indicated electrometrically.

RÉSUMÉ

Une nouvelle méthode est proposée pour le dosage des groupes carboxyles dans le polycaprolactame. Le polymère est dissous dans 2,6-xylénol et chloroforme à 130° et les groupes carboxyles sont titrés potentiométriquement à 30° avec une solution éthanolique d'hydroxyde de potassium. Les résultats sont identiques à ceux qu'on obtient en dissolvant le polymère dans l'alcool benzylique à 175° et en titrant à 135°, l'indicateur étant la phénolphtaleine.

ZUSAMMENFASSUNG

Eine neue Methode zur Bestimmung von Carboxylgruppen in Polycaprolactam wird vorgeschlagen. Das Polymere wird bei 130° in einem Gemisch von 2,6-Xylenol und Chloroform gelöst und die Carboxylgruppen werden potentiometrisch mit aethanolischer Kaliumhydroxydlösung titriert bei 30°. Diese Methode gibt dieselben Ergebnisse wie die Methode bei der das Polymere bei 175° in Benzylalkohol gelöst und bei 135° auf Phenolphthalein titriert wird.

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GAS–LIQUID CHROMATOGRAPHIC ANALYSIS OF C_{10}–C_{16} *n*-PARAFFINS, ISOPARAFFINS AND α-OLEFINS IN A LOW-TEMPERATURE COAL TAR

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INTRODUCTION

The Federal Bureau of Mines is studying the detailed characterization of hydrocarbons in the neutral oil from a low-temperature bituminous coal tar. The work on the aromatic hydrocarbons boiling between 110° and 280° was reported in two previous papers[1,2]. This paper concerns the analysis of some paraffinic and olefinic hydrocarbons boiling between 167° and 287° in the same neutral oil.

Previously, several non-aromatic hydrocarbons were identified in different low-temperature tars by research workers[3–6] using older methods. These hydrocarbons include C_5 to C_{15} *n*-paraffins, C_5 to C_{13} olefins, and C_5 to C_{10} 2-methyl alkanes. However, quantitative estimates were made only for about a dozen compounds in the C_5 to C_{10} range. LEWIS[7] used gas–liquid chromatography to identify the C_9 to C_{22} *n*-paraffins in a low-temperature coal tar by retention time, and mentioned that their quantities were each about 0.04% of the total dry tar. He tentatively identified the C_{10} to C_{17} isoparaffins (2-methyl alkanes), having no reference compounds available, and stated that each of these compounds might total about 0.02% of the tar. In the present work, 14 paraffins and 7 olefins in the C_{10} to C_{16} range were identified positively and the quantity of each compound was determined.

Correlations between logarithms of relative retention and boiling points for the series of C_{10} to C_{16} *n*-paraffins and α-olefins were established. A similar correlation was derived for the corresponding 2-methyl alkane series which made identification of several such compounds possible.

EXPERIMENTAL WORK AND RESULTS

Preparation of non-aromatic hydrocarbon concentrates from the coal tar for gas–liquid chromatography

The non-aromatic hydrocarbon concentrates were obtained from the same neutral oil from a West Virginia bituminous coal tar used in the earlier work on aromatic hydrocarbons. The neutral oil was distilled, and the distillate fractions were each separated into saturates, unsaturates, and aromatics by displacement chromatography on silica gel, as previously described[1,2].

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The data on displacement chromatography of several high-boiling distillate fractions not included in the earlier papers are presented in Table I.

TABLE I

DISPLACEMENT CHROMATOGRAPHIC SEPARATION OF NEUTRAL OIL DISTILLATE FRACTIONS INTO CHEMICAL TYPES

Distillate fraction number[a,b]	*Weight of charge (g)*	*Saturates + some olefins*			*Aromatics + some olefins and some O, S compounds*			*Material retained on column (g)*
		n_D^{20} *range*	*Total weight (g)*	*Number of fractions*	n_D^{20} *range*	*Total weight (g)*	*Number of fractions*	
9*	8.71	1.4570–1.4878	1.46	3	1.5265–1.5938	6.70	14	0.55
10*	8.69	1.4551–1.4710	1.26	3	1.5103–1.5951	6.67	13	0.76
11*	8.34	1.4457–1.4865	1.58	4	1.5184–1.6000	6.09	13	0.67
12*	8.58	1.4391–1.4841	1.88	5	1.5200–1.6008	5.80	14	0.90
13*	8.44	1.4392–1.4790	2.22	6	1.5160–1.6052	5.70	14	0.52
14*	8.62	1.4390–1.4820	1.98	5	1.5128–1.6065	6.19	17	0.45
15*	8.83	1.4473–1.4895	1.50	5	1.5126–1.6112	6.83	20	0.50
16*	3.14	1.4495–1.4669	0.49	2	1.5173–1.5851	2.19	8	0.46

[a] Asterisk designates fractions shown in Table I of ref.[2]
[b] Desorbent: cyclohexanol; column temperature: approximately 100°.

TABLE II

REFRACTIVE INDICES OF DISPLACEMENT CHROMATOGRAPHIC CUTS OF DISTILLATE FRACTION 21, AND PREDICTED CHEMICAL TYPES

Cut No.	n_D^{20}	*Possible chemical type*
1	1.4360	Paraffin
2	1.4407	Paraffin
3	1.4455	Paraffin (major), naphthene (trace)
4	1.4490	Paraffin (major), naphthene (trace)
5	1.4521	Paraffin (major), naphthene (trace)
6	1.4561	Paraffin (major), naphthene (minor)
7	1.4606	Paraffin (major), naphthene (major)
8	1.4591	Paraffin (minor), naphthene (major), olefin (minor)
9	1.4503	Paraffin (trace), naphthene (trace), olefin (major)
10	1.4512	Olefin
11	1.4573	Olefin
12	1.4719	Olefin (major), aromatic (trace)
13–31	1.4948–1.5943	Aromatic

Bureau workers found that on the displacement chromatographic column, the hydrocarbons came out in the following order: paraffins, naphthenes, olefins, cyclic olefins, aromatic hydrocarbons, and oxygenated hydrocarbons. The saturates and unsaturates overlapped only in one cut, which could be recognized by its refractive index. In general, the refractive indices of the naphthenes were slightly higher than those of the paraffins or olefins. The first cut usually contained only paraffins. The point at which naphthenes appeared depended on their concentration: the higher the concentration, the sooner the appearance.

The concentration of naphthenes increased with the number of cuts to a maximum and then dropped quickly when olefins appeared. This change was indicated by a corresponding increase and decrease of the refractive indices of the cuts.

Table II shows the refractive indices of all displacement chromatographic cuts of distillate fraction 21, boiling at 246° to 248° (Table I, ref. 1). The refractive index increases to a maximum at cut 7 and decreases in cut 8 where olefins appeared. Therefore, cut 8 was considered to be the intermediate fraction between saturates and unsaturates. This was subsequently verified by gas–liquid chromatography.

Gas–liquid chromatography of non-aromatic hydrocarbons

The apparatus used in this work was a Perkin-Elmer model 154C Vapor Fractometer, as described previously[1,2]. The peak areas on the chromatograms were measured with a planimeter. Four columns, each containing one of four different stationary phases, namely, Apiezon L grease, silicone rubber, Dow Corning silicone oil 710 (a phenyl silicon polymer) and polyphenyl ether, *i.e.*, *m*-bis(*m*-phenoxyphenoxy)benzene, were evaluated at different temperatures. Each column was 15 ft. long × 1/4 in. o.d. aluminum tubing filled with a packing made by coating 30–60 mesh fire brick with 25% by weight of liquid phase. The separations of paraffins and olefins on the non-polar liquids, namely, Apiezon L grease and silicone rubber, were made according to boiling points and were only fair. Silicone oil 710 separated the paraffins and olefins from the residual aromatics and gave a good separation of the individual compounds from each other among the two non-aromatic types. However, this substrate came out of the column even at 140°, making it impossible to get usable infrared spectra of collected components. The other polar compound, polyphenyl ether, gave an excellent separation according to compound type with the residual aromatics being held on the column much longer than the paraffins and olefins. Olefins were eluted after paraffins with the same boiling range, while α-olefins emerged ahead of the other types of unsaturates. However, *cis*- and *trans*-olefins were not resolved on the 15-ft. column. Polyphenyl ether was not eluted along with the components even at 220° and was selected for the work reported here. The polyphenyl ether column was cured at 170° by blowing helium through for two days before use.

Column temperatures of 170° and 220° were selected for analyzing fractions boiling at 163° to 240° and 240° to 287°, respectively. No change of retention time for pure compounds on this column at 170° was noticed for a period of 6 months. However, a slight decrease in retention time was observed at 220° after a period of 10 weeks. Therefore, the 220° column was checked every three weeks with standard mixtures of known components.

Helium was used as the carrier gas with a flow rate of 100 ml/min at the inlet; the inlet pressure was 30 lb./in.^{2} and the outlet pressure was atmospheric. The potential for the detector was 8 V. Throughout the work the temperature stayed within ±0.1°, and the helium pressure and the voltage of the detector were constant. Referring to *n*-undecane at 170° and to *n*-tridecane at 220°, the number of theoretical plates was 2230 and 2050, respectively[8].

Identification of separated components

The retention times for some paraffins and olefins were obtained, and their relative retentions (either time or volume) referred to *n*-undecane at 170° and to *n*-tridecane

at 220° are shown in Table III along with their boiling points. API standard samples were used insofar as they were available.

Identification of individual *n*-paraffins and α-olefins in the non-aromatic cuts was based primarily on retention time. Infra-red spectra, the components being collected as previously described[1], served mostly for simply confirming the general chemical types. Whereas certain chemical types such as *n*-paraffins, isoparaffins, and α-olefins can be easily differentiated by their characteristic infrared bands, individual members

TABLE III

BOILING POINTS, RELATIVE RETENTIONS AND CALIBRATION FACTORS (f_c) OF SOME PARAFFINS AND OLEFINS

Compound	Boiling point (°C/760 mm)[a]	At 170°		At 220°	
		Relative retention referred to n-undecane[b]	f_c[c]	Relative retention referred to n-tridecane[b]	f_c[c]
n-Decane	174.123	0.613	0.99	0.310	—
n-Undecane	195.890	1.000	1.00	0.469	0.98
n-Dodecane	216.278	1.616	0.98	0.681	0.99
n-Tridecane	235.434	2.605	0.96	1.000	1.00
n-Tetradecane	253.515	4.185	1.03	1.468	0.99
n-Pentadecane	270.614	6.713	—	2.138	0.97
n-Hexadecane	286.793	—	—	3.125	1.04
n-Heptadecane	302.15	—	—	4.614	—
Trans-decalin	187.25	1.691	1.14	0.803	1.18
Cis-decalin	195.69	2.262		1.028	
Dicyclohexyl	235	5.340	—	2.116	1.18
2-Methyl nonane	167.00	0.485[d]	—	—	—
2-Methyl decane	189.19	0.815	0.95	0.389	0.94
2-Methyl undecane	210.0	1.316[d]	—	0.576[d]	—
2-Methyl dodecane	229.5	2.110[d]	—	0.853[d]	—
2-Methyl tridecane	247.9	3.400[d]	—	1.229[d]	—
2-Methyl tetradecane	265.2	—	—	1.780[d]	—
2-Methyl pentadecane	281.6	—	—	2.580[d]	—
1-Octene	121.280	0.241	1.01	—	—
Trans-4-octene	122.25	0.235	1.08	—	—
1-Decene	170.570	0.692	0.98	—	—
1-Undecene	192.671	1.115	0.97	0.510	1.01
1-Dodecene	213.357	1.809	1.02	0.747	1.01
1-Tridecene	232.780	2.920	1.01	1.094	0.97
1-Tetradecene	251.100	4.686	—	1.602	1.02
1-Pentadecene	268.394	7.512	—	2.333	0.99
1-Hexadecene	284.873	—	—	3.425	1.03

[a] All values from API Research Project 44, *Selected Values of Properties of Hydrocarbons and Related Compounds*, Carnegie Institute of Technology, Pittsburgh, Pa., with the exception of dicyclohexyl from G. EGLOFF, *Physical Constants of Hydrocarbons*, Reinhold Publishing Corp., New York, 1957.

[b] Dead volume corrected.

[c] Defined in eqn. (1).

[d] The relative retentions of these compounds were determined from tar components identified by boiling points and I.R.

of each chemical type absorb qualitatively at almost identical frequencies, thus making individual identification very difficult. However, the unexpected simplicity of the chromatograms made identification of individual *n*-paraffins, isoparaffins and α-olefins easy. There are a number of theoretically possible isoparaffins for each molecular weight, the boiling points and retention times of these all being less than for the *n*-paraffin of the same molecular weight. Nevertheless, the chromatograms representing the entire boiling range for this work all showed a single, sharp, symmetrical peak preceding the *n*-paraffin peak. A few samples might give an isoparaffin peak that was produced by two or three isoparaffins, but the possibility of this occurring over a wide molecular weight range appears remote since the number of theoretically possible isomers increases essentially exponentially with molecular weight. The infrared spectra of the components producing the isoparaffin peak were very nearly identical. The members of any single type of isoparaffin show this extensive similarity of spectra, but there are significant differences between different types of isoparaffins.

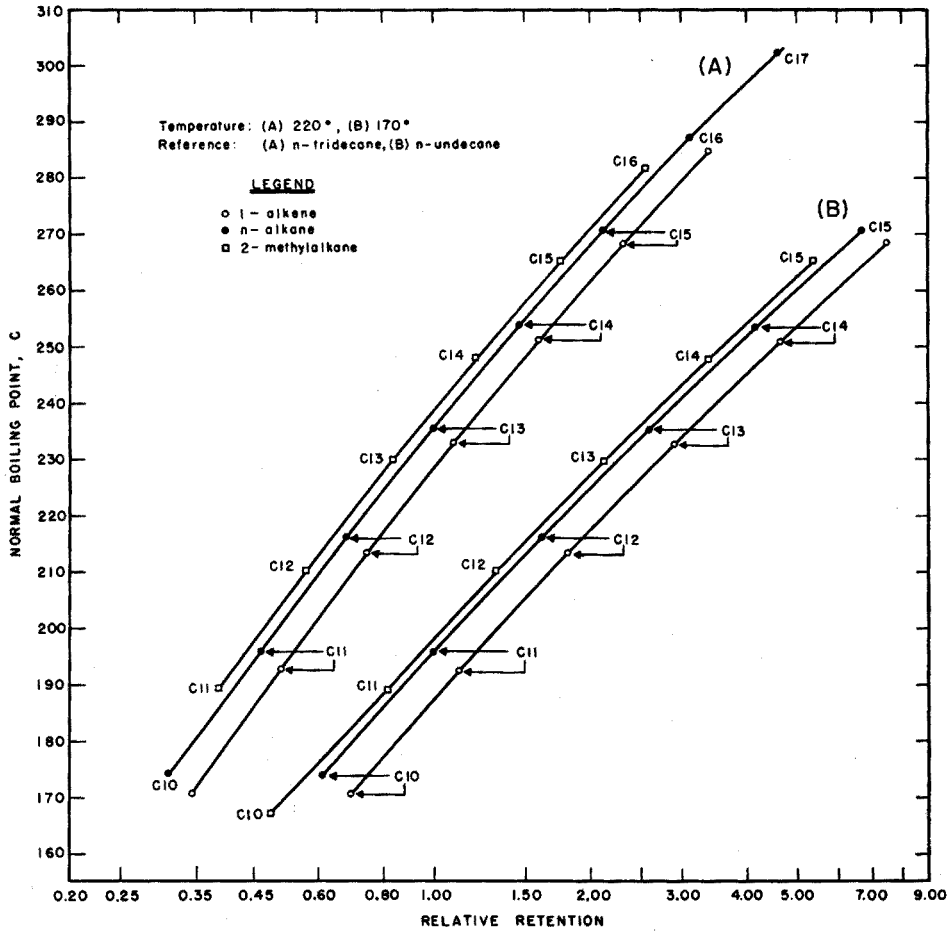

Fig. 1. Correlation between boiling points and relative retentions of C_{10}–C_{16} *n*-paraffins, isoparaffins and α-olefins on polyphenyl ether.

It is extremely unlikely that mixtures of types of isoparaffins covering a wide boiling range could all have nearly identical spectra.

With the exception of 2-methyl decane, authentic specimens of the isoparaffins (the 2-methyl alkanes) were not available, so that a somewhat different approach had to be used. It was observed that when the logarithms of the relative retentions of the C_{10} through C_{16} *n*-paraffins and α-olefins were plotted against their respective boiling points, two parallel, slightly curved lines were obtained. It was assumed that the curve foi the 2-methyl alkanes would likewise be parallel to the curves for the *n*-paraffins and α-olefins, and would pass through the one known point for 2-methyl decane. Fig. 1 shows the curves for these three chemical types at 170° and 220°. A comprehensive study by research workers in Belgium, which came to our attention after the completion of our work, has shown that the 2-methyl alkanes, 3-methyl alkanes, 4-methyl alkanes, 2,2-dimethyl alkanes and 2,2'-dimethyl alkanes each have their own distinct and separate curve[9]. It was demonstrated that in spite of the closeness in boiling point of isomeric isoparaffins, the presence or absence of a particular type of isoparaffin can be established. The 2-methyl alkanes were found to account for essentially all of the isoparaffins in their low-temperature tar.

In addition to 2-methyl decane, which was identified through the retention time of the authentic specimen, 6 additional 2-methyl alkanes were identified by means of the appropriate curve shown in Fig. 1. Table IV presents the comparison of the boiling points of certain components, as obtained from relative retentions and this curve, with boiling points of 2-methyl alkanes obtained from the literature. The identities of these six 2-methyl alkanes were substantiated by infrared spectroscopy.

TABLE IV

IDENTIFICATION OF SIX 2-METHYL ALKANES BY MEANS OF THE CORRELATION BETWEEN BOILING POINTS AND RELATIVE RETENTIONS

Compound	*Boiling point (°C)*	
	From the literature	*From the relative retentions and the correlation curve*
2-Methyl nonane	167.0	167.2[a]
2-Methyl undecane	210.0	210.0[a], 210.0[b]
2-Methyl dodecane	229.5	229.1[a], 230.0[b]
2-Methyl tridecane	247.9	247.8[a], 248.1[b]
2-Methyl tetradecane	265.2	265.3[b]
2-Methyl pentadecane	281.6	281.2[b]

[a] Column temperature, 170°
[b] Column temperature, 220°

According to BELLAMY[10], in addition to the CH stretching bands for paraffins at 2926 cm^{-1} to 2853 cm^{-1} and near 1465 cm^{-1}, 2-methyl alkanes, because of the isopropyl group, should show a medium strong band at 1170 $\pm$ 5 cm^{-1} and two split bands at 1385–1380 cm^{-1} and at 1370–1365 cm^{-1}. The infrared spectra of the 6 2-methyl alkanes all showed the characteristic bands for paraffins and, in addition, a medium strong band at or near 1168 cm^{-1} and two split bands at or near 1378 cm^{-1} and 1367 cm^{-1}.

In Fig. 2, three gas–liquid chromatograms are given as examples. These were produced from three consecutive displacement chromatographic cuts (7, 8 and 9), obtained from distillate fraction 21, as shown in Table II. Peaks 1, 2, 3 and 5 were readily shown to be produced by 2-methyl tridecane, *n*-tetradecane, 2-methyl tetradecane and 1-tetradecene, respectively. The component producing peak 4 was shown to be a binuclear naphthene through infrared spectral-structural correlations. All

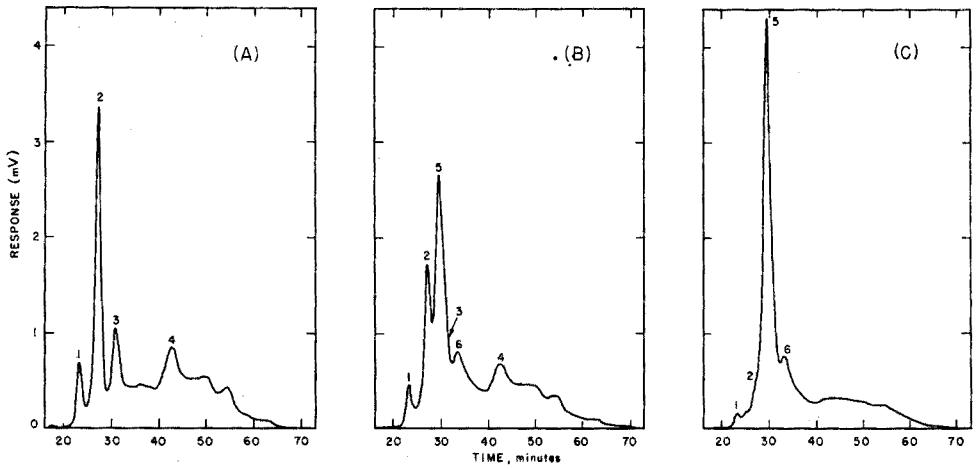

Fig. 2. Gas–liquid chromatograms at 220° on polyphenyl ether of three consecutive displacement chromatographic cuts of distillate fraction 21. Legend: (A) Cut 7, n_D^{20} 1.4606, sample size 8 ml (B) Cut 8, n_D^{20} 1.4591, sample size 8.5 ml; (C) Cut 9, n_D^{20} 1.4503, sample size 6 ml. Peak identification: 1, 2-methyl tridecane; 2, *n*-tetradecane; 3, 2-methyl tetradecane; 4, binuclear naphthene; 5, 1-tetradecene; 6, *trans*-olefin.

6-membered saturated cyclic hydrocarbons show characteristic frequencies in the ranges 1005–952 cm^{-1} and 1055–1000 cm^{-1} originating from ring deformations[10]. It can be seen that *trans*-decalin absorbs strongly at 1057 cm^{-1}, 1029 cm^{-1}, 987 cm^{-1} and 971 cm^{-1}, *cis*-decalin at 1011 cm^{-1}, 978 cm^{-1} and 969 cm^{-1} and cyclohexyl cyclohexane near 995 cm^{-1} and at 954 cm^{-1}. These absorptions are believed to be due to ring deformations and to be characteristic of binuclear naphthenes. Other characteristic frequencies can be observed for these three compounds in the range 900–825 cm^{-1}. The component producing peak 4 absorbed strongly between 1050 and 950 cm^{-1} and between 900 and 850 cm^{-1}, in addition to having CH stretching bands at approximately 2926 cm^{-1} and 2853 cm^{-1}. This component was, therefore, considered to be an alkyl binuclear naphthene. Several other components having similar absorption bands were found in the saturate cuts of the other distillate fractions.

The component producing peak 6 was shown to be a *trans*-olefin. Its infrared spectrum had a medium weak band near 1670 cm^{-1} and a very strong band at 965 cm^{-1}. These are considered to be characteristic of *trans*-olefins[10]. Since this *trans*-olefin was eluted immediately after the C_{14} α-olefin (peak 5), it is possible that this component is one of the C_{14} *trans*-isomers. Several other components emerging immediately after other α-olefins were likewise considered to be *trans*-olefins.

Cut 8 (Fig. 2, B) was the only cut from fraction 21 containing both saturates and

unsaturates in high concentrations. Complete agreement cannot be expected between chemical types predicted from refractive index (Table II) and the actual constituents found by gas–liquid chromatography (Fig. 2) because, as previously indicated, there is no way to distinguish naphthenes from mixtures of paraffins and olefins by refractive index. Gas–liquid chromatography, followed by infrared spectrophotometry of the chromatographic fractions, showed that cuts 1 through 7 consisted entirely of saturates with an increasing naphthene content with each increasing cut number. Cuts 9 through 11 contained mainly α-olefins and some *trans*-olefins. Cut 12 contained olefins, possibly cyclic, and a trace of aromatics.

Quantitative analysis of individual paraffins and olefins

The internal standard method, described previously[1,2], was used:

$$f_C = A_s W_c / A_c W_s \qquad (1)$$

where A_s and A_c are the areas for the internal standard and the component in the

TABLE V

ANALYSIS OF INDIVIDUAL C_{10}–C_{16} *n*-PARAFFINS, ISOPARAFFINS AND α-OLEFINS IN NEUTRAL OIL DISTILLATE FRACTIONS

Compounds identified	*Distillate fractions*	*Method of identification*	*Total weight (g)*	*Wt.% in neutral oil*[a]
n-Decane	1,2	Rel. retention and I.R.[b]	0.2481	0.036
n-Undecane	3–6	Rel. retention and I.R.[b]	1.4842	0.213
n-Dodecane	7–14	Rel. retention and I.R.[b]	6.6226	0.949
n-Tridecane	12–20	Rel. retention and I.R.[b]	11.2807	1.62
n-Tetradecane	20–26	Rel. retention and I.R.[b]	5.5026	0.788
n-Pentadecane	25–29 1*–8*[c]	Rel. retention and I.R.[b]	7.3638	1.06
n-Hexadecane	9*–16*	Rel. retention and I.R.[b]	3.7244	0.534
			Total:	5.200
2-Methyl nonane	1,2	B.p. and I.R.-structural correlation	0.1551	0.022
2-Methyl decane	1–5	Rel. retention and I.R.[b]	0.2356	0.034
2-Methyl undecane	6–11	B.p. and I.R.-structural correlation	0.8742	0.125
2-Methyl dodecane	12–17	B.p. and I.R.-structural correlation	1.4344	0.206
2-Methyl tridecane	19–23	B.p. and I.R.-structural correlation	1.4000	0.201
2-Methyl tetradecane	21–29, 1*–3*	B.p. and I.R.-structural correlation	2.9188	0.418
2-Methyl pentadecane	10*–13*	B.p. and I.R.-structural correlation	0.1367	0.020
			Total:	1.026
1-Decene	1,2	Rel. retention and I.R.[b]	0.1595	0.023
1-Undecene	3–6	Rel. retention and I.R.[b]	1.1871	0.170
1-Dodecene	7–14	Rel. retention and I.R.[b]	1.4485	0.208
1-Tridecene	12–19	Rel. retention and I.R.[b]	4.5744	0.655
1-Tetradecene	20–25	Rel. retention and I.R.[b]	4.3582	0.624
1-Pentadecene	25–29, 1*–5*	Rel. retention and I.R.[b]	2.8693	0.411
1-Hexadecene	9*–16*	Rel. retention and I.R.[b]	2.1243	0.304
			Total:	2.395

[a] Total neutral oil distilling up to about 360°, representing 16.92 wt.% of the total tar.
[b] Infrared spectra of these compounds were obtained in this laboratory.
[c] Asterisk (*) designates fractions shown in Table I of the previous report[2]; others are shown in Table I of the first report[1].

sample, and W_c and W_s are the weight-percentages of the component and the standard. *n*-Undecane and *n*-tridecane were selected as the standards at 170° and 220° respectively. The f_C values for some saturates and unsaturates are shown in Table III. The f_C values for *n*-paraffins and α-olefins range from 0.94 to 1.04 with an average close to 1. Therefore, when no other types were present in the sample, the calculations could be simplified by using the area-percents of the peaks for the weight-percents of the components. However, when the sample contained branched-chain paraffins and olefins, naphthenes, and cyclic olefins, the individual f_C values were used. The f_C value of 2-methyl decane was used for those 2-methyl alkanes for which no authentic specimens were available.

The individual *n*-paraffins, isoparaffins, and α-olefins found in the neutral oil, and their amounts, are presented in Table V.

The quantities of total naphthenes and total *trans*-olefins were estimated to be only 2.5% and 0.5%, respectively, of the neutral oil. The quantities of total *n*-paraffins, total isoparaffins and total α-olefins, however, were determined to be 5.200%, 1.026% and 2.395%, respectively, of the neutral oil. Thus, about 3/4 of the saturates and olefins were made up of the 21 individual compounds that were identified.

SUMMARY

21 C_{10}–C_{16} hydrocarbons, 7 each of *n*-paraffins, 2-methyl alkanes and α-olefins, were identified in a low-temperature bituminous coal tar by means of gas–liquid chromatography. Quantitative determinations were made on all of these constituents. It was found that the curves for the plots of logarithms of relative retention against normal boiling points for C_{10}–C_{16} *n*-paraffins and α-olefins are parallel. A similar parallel curve for the 2-methyl alkane series was derived, using the known point for 2-methyl decane. This correlation curve was used for the identification of several 2-methyl alkanes. Naphthenes and *trans*-olefins were found in small amounts.

RÉSUMÉ

21 hydrocarbures (C_{10}–C_{16}: *n*-paraffines, méthyl-2-alcanes, α-oléfines) ont pu être identifiés dans des goudrons de charbon bitumineux, par chromatographie gaz–liquide. Des dosages de chacun de ces constituants ont été effectués. On a décelé également des naphtènes et des *trans*-oléfines, en faibles teneurs.

ZUSAMMENFASSUNG

In Bitumenteer konnten mit Hilfe der Gaschromatographie 21 Kohlenwasserstoffe im Bereich C_{10}–C_{16}, darunter *n*-Paraffine, 2-Methylalkane und α-Olefine identifiziert werden. Es wurden ferner Naphtene und trans-Olefine nachgewiesen .

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CHROMATOGRAPHIC SEPARATION AND DETERMINATION OF FRUIT ACIDS

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The successful application of salting-out chromatography to the analysis of mixtures of alcohols[1], amines[2], aldehydes[3], ketones[3], and ethers[4] led to an unsuccessful attempt to apply this method to the principal acids of fruit (citric, malic and tartaric). The distribution ratios, C, of these acids with Dowex 50 were too nearly equal to permit a satisfactory separation[4]. When it was found that partly sulfonated polystyrene resins gave better separations than the fully sulfonated resins[5,6], it seemed advisable to try these low-capacity resins in the salting-out chromatography of the fruit acids.

Although the procedure for the separation of these acids by ion-exchange chromatography[7] has served satisfactorily in some laboratories, complaints[8] have been received that the permanganometric method for the analysis of the eluate fractions

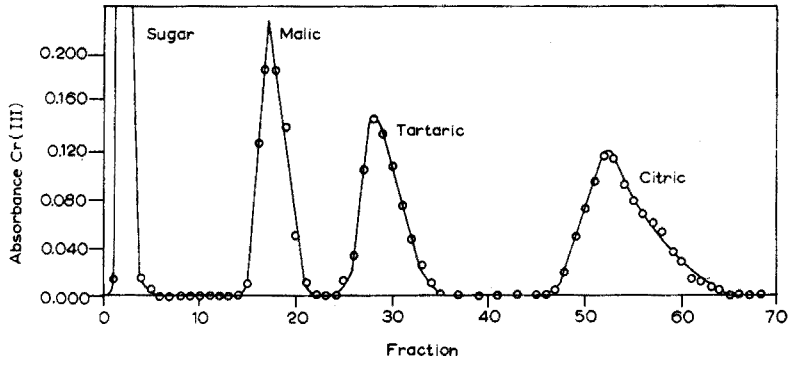

Fig. 1. Elution graph of sugar and fruit acids. Column: 10.0 cm × 0.95 cm² of Dowex 1-X8, 200–400 mesh. Eluent 2.0 M acetic acid +0.40 M sodium acetate. Flow rate: 0.50 cm/min. Fractions: 2.92 ml.

is not reliable. The spectrophotometric method with dichromate[9] has been found to be very reliable[1–6] but is not applicable in the presence of nitrate, which was used as the eluent in the separation of the fruit acids by ion-exchange chromatography. These facts furnished an additional incentive for the re-examination of the separation of the fruit acids.

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A method[10] was developed for the quantitative separation by salting-out chromatography of oxalic, tartaric, malic, citric, and lactic acids by elution with a sulfate–bisulfate buffer through a 100-cm column of an incompletely sulfonated polystyrene (capacity = 4.1 mequiv. per g, 4% crosslinked). The method suffered from several disadvantages; the worst of these was a very slow flow rate that required an elution period of five days.

Attention was then turned toward anion-exchange chromatography with various buffer systems. Two fairly rapid methods for the quantitative separation of malic, tartaric and citric acids were developed with Dowex 1-X8 as the stationary phase. In one method, the eluent was 0.15 *M* phosphoric acid plus 2.0 *M* monosodium phosphate. The major disadvantage of this method is that the elution graph of tartaric acid (the first of the fruit acids) overlaps badly the graph of the sugars.

With an eluent of 2.0 *M* acetic acid and 0.40 *M* sodium acetate, quantitative separation of the three fruit acids from each other and from the sugars was achieved (Fig. 1). Since acetic acid is much more resistant to oxidation than the fruit acids, it was possible to determine the latter in the eluate fractions by a slight modification of the dichromate procedure[9] without any interference from the acetic acid. The details of this method are given in the next section. Variations in the composition of the acetate eluent affected the positions of the peaks of the fruit acids in accordance with the equations previously published[11].

EXPERIMENTAL

Apparatus and reagents

Prepare the eluent solution to be 0.40 *M* with sodium acetate and 2.0 *M* with acetic acid. The pH should be 4.0 ± 0.1. Prepare the solution of sodium dichromate in concentrated sulfuric acid as described elsewhere[9].

Slurry Dowex 1-X8, 200–400 mesh, with water. Let it settle about 5 min; then pour off the supernatant suspension of the very fine particles. Repeat this procedure several times until most of the fines are removed. Pour a slurry of the resin into a glass tube, 0.95 cm^2 in internal cross-sectional area, provided with a sintered-glass filter disk of medium porosity and a stopcock or pinchclamp. The height of the resin column should now be a little more than 10.0 cm. Pass the eluent through the column until the resin is completely in the acetate form (negative test for chloride in the effluent). If necessary, adjust the height of resin to 10.0 cm.

Preparation of fruit juices

Cut the fruit into suitable pieces and put it on a filter mat of 6 or 8 layers of surgical gauze on a Buchner funnel. Apply vacuum and press the fruit with a Petri dish. Centrifuge the filtrate to remove finely divided solids and store the supernatant juice in a refrigerator until it is to be used.

Pipet a suitable volume of the juice into a small beaker and add 5 *M* sodium hydroxide to a pH of 4.0, measured with a pH meter. Transfer to a volumetric flask and dilute to the mark with eluent. The pipet and flask should be chosen so that the concentration of the most abundant acid is between 4 and 9 mg per ml.

Elution

Drain the surplus eluent from the column until the liquid level is about 1 mm above

the top of the resin. Pipet 1.000 ml of sample solution into the column, taking care not to agitate the resin. Drain the liquid again to within 1 mm of the resin. Rinse the inside wall of the chromatographic tube with about 1 ml of eluent and again drain the liquid almost to the resin. Repeat this rinsing and draining twice more. Connect a supply of eluent to the top of the chromatographic column with an air-tight stopper. Maintain a flow rate of 0.50 ± 0.10 cm per min (0.47 ± 0.09 ml per min) by adjusting the hydrostatic head or the stopcock.

It is then necessary to collect successive fractions of 37.5, 30.0, 50.0, 12.5 and 75.0 ml, which will contain respectively the sugars, malic acid, tartaric acid, waste and citric acid. This is done conveniently as follows: Collect the sugar in a 50-ml volumetric flask to which 12.5 ml of eluent has been added from a buret. Collect the malic acid similarly but add 20.0 ml of eluent to the flask. Use a dry 50-ml flask for the tartaric acid, a 25-ml flask containing 12.5 ml of eluent for the waste and a 100-ml flask containing 25.0 ml of water for the citric acid.

Spectrophotometric determinations

Shake the volumetric flasks containing the sugars, malic acid and tartaric acid. Pipet 20.00 ml of each solution into separate 100-ml flasks. Pipet 5.00 ml of water and 20.00 ml of dichromate in sulfuric acid into each flask. Heat them in a bath of boiling water for 30 min. Then cool them to room temperature in a cold-water bath. Read the absorbances at 591 mμ in 100-mm cells, using as a reference a solution prepared by treating 20.00 ml of eluent in exactly the same manner. A Beckman DU spectrophotometer is recommended.

Determine the citric acid similarly but use 25.00 ml of the eluate fraction, no water and 20.00 ml of the dichromate solution.

Convert the absorbance to mg of sugar or acid from calibration graphs prepared as follows: Prepare a solution of 200.0 mg of malic acid in 100.0 ml of eluent. Pipet aliquots of 1.000, 2.000, 3.000 and 4.000 ml into separate 50-ml volumetric flasks and dilute to the mark with eluent. Treat 20.00 ml of each of these solutions exactly as described above for the fraction of eluate containing the malic acid. Prepare calibration graphs for the sugar (using dextrose) and for the tartaric acid in the same manner. Prepare a standard solution of citric acid containing 200.0 mg in 100.0 ml of eluent. Pipet aliquots of 2.000, 4.000, 6.000 and 8.000 ml into separate 100-ml volumetric flasks. Add 25.00 ml of water to each flask and dilute to the mark with eluent. Treat 25.00 ml of each of these solutions exactly as described above for the fraction of eluate containing the citric acid. All the graphs of absorbance *vs.* concentration of acid or dextrose were linear within the specified range.

Since the nature of the sugars differs from fruit to fruit, the foregoing procedure may not determine the actual concentration of sugar (mg/ml) in the juice but rather yields the concentration of dextrose equivalent to the total fruit sugar in reducing capacity according to the recommended method. Although no experimental comparisons of the reducing capacities of the various sugars were performed, it is likely that the several sugars found in fruit have very nearly the same reducing capacity per g[9].

RESULTS AND DISCUSSION

The analytical procedure was first tested with five standard solutions prepared by

weighing the pure solutes. These results are presented in Table I. The mean recovery of all 11 determinations was 100.3%, indicating good accuracy. The standard deviation of the recovery was 1.0%, indicating good precision.

Then four samples of fruit juice were analyzed in duplicate. In some of the determinations, known amounts of fruit acid were added as indicated in Table II. The

TABLE I

ANALYSIS OF STANDARD SOLUTIONS

Soln. No.	Dextrose		Malic acid		Tartaric acid		Citric acid	
	Taken mg	Recovery %	Taken mg	Recovery %	Taken mg	Recovery %	Taken mg	Recovery %
1	2.48	100.4						
2	2.67	100.0					8.04	100.0
3	25.5	97.6	8.68	101.0				
4	103.2	100.7			9.86	100.2		
5	101.1	100.1	9.31	101.3	6.09	101.5	6.32	100.6

TABLE II

ANALYSIS OF FRUIT JUICES

(The results are expressed as mg/ml)

Fruit	Sugar		Malic acid		Tartaric acid		Citric acid	
	Added	Found	Added	Found	Added	Found	Added	Found
Lemon	0.0	17.7	0.0	3.9	0.0	0.0	0.0	51.7
	0.0	17.2	82.5	84.5[a]	79.7	78.5	0.0	52.8
Mean		17.5						52.2
Apple	0	208	0.00	5.53	0.00	0.00	0.00	0.00
	0	207	0.00	5.60	6.40	6.56	6.71	6.60
Mean		208		5.57				
Peach	0	124	0.00	5.89	0.00	0.00	0.00	4.14
	0	118	0.00	5.87	7.01	7.03	0.00	4.33
Mean		121		5.88				4.24
Seedless grape	0	144	0.00	5.13	0.00	7.22	0.00	0.00
	0	143	0.00	5.00	0.00	6.98	6.78	6.72
Mean		144		5.06		7.10		

[a] This figure represents the quantity originally in the juice plus the quantity added.

average difference between the duplicates was 2 mg per ml for sugar, 0.09 for malic acid exclusive of the lemon juice, 0.22 for tartaric acid and 0.6 for citric acid. When tartaric acid was added to a juice containing none of this acid, the mean recoveries were 100.4% with a standard deviation of 1.9%. The similar figures for the recovery of citric acid were 98.8% and 0.4%. These figures confirm satisfactorily the accuracy and precision predicted from the analyses of standard solutions.

The occurrence in a fruit of an acid other than malic, tartaric and citric would not be detected by this method unless the elution peak happened to occur between the peaks of Fig. 1. Thus the unsuspected acid would cause a positive error in the deter-

mination of malic, tartaric or citric acid. However, this is not a serious disadvantage because significant quantities of acids other than these three are rarely found in fruit.

The elution requires 7 h, about the same as SCHENKER's[7] elution. The simplicity and reliability of the spectrophotometric method of analyzing the fractions of eluate are marked advantages of this method in comparison with SCHENKER's. In addition, the recommended method serves to determine the sugar in the juice. This method is much more rapid and accurate than the classical procedures such as the pentabromoacetone method[12] for the determination of citric acid.

Since ion-exchange resins vary appreciably from batch to batch, it cannot be guaranteed that strict adherence to the recommended elution procedure will always yield quantitative separations of the fruit acids. An analyst using a different batch of Dowex 1-X8 may have to make minor changes in the elution conditions such as the column height or the volumes of eluate containing the isolated acids.

SUMMARY

A method is described for the determination of malic, tartaric and citric acids and sugar in fruit juices. It consists of the separation of these constituents by ion-exchange chromatography through a column of Dowex 1-X8 with an acetate buffer as eluent, treatment of aliquots of the separated constituents with dichromate and sulfuric acid and measurement of the absorbance of the resultant green chromium(III).

RÉSUMÉ

Une méthode est décrite pour le dosage des acides malique, tartrique, citrique et du sucre dans les jus de fruits. La séparation s'effectue par chromatographie au moyen d'échangeur d'ions (Dowex 1-X8) et l'analyse par spectrophotométrie, après traitement au dichromate et à l'acide sulfurique.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Äpfel-, Wein -und Zitronensäure sowie des Zuckergehaltes von Fruchtsäften. Die Trennung erfolgt durch Ionenaustauscher-Chromatographie. Die Eluate werden mit Bichromat–Schwefelsäure behandelt und die Absorption der entstandenen grünen Chrom(III)-lösung gemessen.

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SPOT TEST DETECTION OF TAURINE THROUGH DEMASKING AND PYROLYTIC EFFECTS*

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Tests for taurine which are almost specific can be based on the application of recently observed pyrolytic effects[1].

All kinds of compounds containing free, even faintly, acidic groups yield hydrogen cyanide when heated to 160° with mercury(II) cyanide:

$$Hg(CN)_2 + 2HX \rightarrow HgX_2 + 2HCN \qquad (1)$$

Aliphatic sulfonic acids produce sulfur dioxide when heated to 200° with molten benzoin (m.p. 137°) through the redox reaction in which benzoin functions as hydrogen donor[2]:

$$RSO_3H + C_6H_5CHOHCOC_6H_5 \rightarrow RH + C_6H_5COCOC_6H_5 + H_2O + SO_2 \qquad (2)$$

The resulting hydrogen cyanide or sulfur dioxide can be readily detected in the gas phase through the color reaction with copper acetate–benzidine acetate[3] or ferri-ferricyanide solution[4]. The indicator turns blue in either instance. Although taurine (2-aminomethanesulfonic acid) contains an aliphatically linked sulfonic acid group, it does not undergo the pyrolysis reactions (1) and (2). This irregular behavior may be attributed to the fact that the reactivity of the sulfonic acid group of taurine is dependent on the isomerization equilibrium

$$\underset{\text{A}}{\begin{matrix}CH_2\text{—}NH_2\\ |\\ CH_2\text{—}SO_3H\end{matrix}} \rightleftharpoons \underset{\text{B}}{\begin{matrix}CH_2\text{—}NH_3^+\\ |\\ CH_2\text{—}SO_3^-\end{matrix}}$$

This equilibrium lies so far toward the side of the ammonium salt form B that the content of the sulfonic acid form A is not adequate to enter into the reactions (1) or (2). In other words, the sulfonic acid group is masked through coordination on the amino group.

It has been found that the sulfonic acid form A can be removed from the isomerism equilibrium by fuming the taurine with formaldehyde. The following condensation reaction then occurs with constant delivery of the A form:

$$CH_2O + \begin{matrix}CH_2\text{—}NH_2\\ |\\ CH_2\text{—}SO_3H\end{matrix} \rightarrow \begin{matrix}CH_2\text{—}N{=}CH_2\\ |\\ CH_2\text{—}SO_3H\end{matrix} \qquad (3)$$

* Translated by RALPH E. OESPER, University of Cincinnati.

Since the basicity of the $-N=CH_2$ group is not sufficient for the formation of a salt, a demasking of the sulfonic acid group is accomplished through reaction (3). Consequently, we are dealing here in principle with a demasking of the type utilized in the SÖRENSEN formol titration of aminocarboxylic acids[5]. It should be noted that the demasking of the sulfonic acid group of taurine can also be brought about by dry-heating this compound with solid paraformaldehyde, which volatilizes during the procedure.

The combining of the demasking reaction (3) with the pyrolysis reactions (1) and (2) makes it possible to detect taurine within the technique of spot test analysis. If the pyrolytic evolution of hydrogen cyanide is employed, after the demasking with formaldehyde as outlined in Procedure I, it should be noted that aminocarboxylic acids may not be present, since they behave in the same manner as taurine. Similarly, no acidic compounds should be present if they react directly with mercury(II) cyanide to produce hydrogen cyanide when the mixture is dry-heated. A preliminary test with these possibilities in mind is definitely in order, before the specimen is subjected to the tests described here. Procedure II in which sulfur dioxide is split out following demasking of the sulfonic acid group with formaldehyde is the more unequivocal. Interference is offered only by the presence of aliphatic sulfonic acids and by compounds containing sulfhydryl groups. Their absence can be determined by a preliminary test with fused benzoin.

PROCEDURE I

A micro test tube is used. One drop of the test solution is taken to dryness along with 1 drop of formalin, or the evaporation residue of 1 drop of the test solution is mixed with several cg of paraformaldehyde and heated to 140° in an oven to insure complete removal of the paraformaldehyde. Several cg of mercury(II) cyanide are mixed in and the mouth of the test tube is covered with a disk of filter paper moistened with copper acetate–benzidine acetate solution. The test tube is immersed to a depth of about 0.5 cm in a glycerol bath which has been preheated to 160°. The development of a blue stain on the reagent paper indicates a positive response.

Reagent solution

(*a*) 2.86 g copper acetate in 1 l of water; (*b*) 675 ml of a water solution of benzidine acetate saturated at room temperature plus 525 ml of water. Solutions (*a*) and (*b*) are best stored separately in well-stoppered dark bottles. When needed, the reagent solution should be freshly prepared by mixing equal volumes of (*a*) and (*b*).

Limit of identification: 5 μg taurine.

PROCEDURE II

The demasking is conducted as described in Procedure I. Several cg of benzoin are added, and the test tube is placed in a glycerol bath pre-heated to 130°. The depth of the immersion is approximately 0.5 cm. The open end of the test tube is covered with a disk of filter paper moistened with ferri–ferricyanide solution. The temperature is then increased to around 180°. A positive response is shown by the appearance of a blue stain on the reagent paper.

Reagent solution

0.08 g ferric chloride and 0.1 g potassium ferricyanide in 100 ml water.

Limit of identification: 10 μg taurine.

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SUMMARY

A test for taurine is described based on demasking of the inner-complex-bound sulfonic acid group by formaldehyde followed by pyrolysis reactions with mercury(II) cyanide or benzoin. The resulting hydrogen cyanide or sulfur dioxide can be detected in the gas phase by familiar color reactions. All the reactions may be conducted within the limits of spot test analysis. Microchemical limits of identification are attained.

RÉSUMÉ

L'auteur propose une réaction pour l'identification de la taurine. Elle est basée sur un ,,démasquage" au moyen de formaldéhyde, suivi d'une pyrolyse avec cyanure de mercure(II) ou benzoïne. L'acide cyanhydrique ou l'acide sulfureux formés sont décelés par les réactions colorées habituelles.

ZUSAMMENFASSUNG

Beschreibung einer Tüpfelprobe zum Nachweis von Taurin. Sie beruht auf der Demaskierung der Sulfosäuregruppe mit Formaldehyd und Nachweis des bei der pyrolytischen Zersetzung in Gegenwart von Quecksilber-(II)-cyanid gebildeten Blausäure. Als Variation wird die pyrolytische Zersetzung in Gegenwart von Benzoin und Nachweis des dabei gebildeten Schwefeldioxyds beschrieben.

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MICROANALYSIS WITH THE AID OF ION-EXCHANGE RESINS

XIX[1]. DETECTION OF NANOGRAM AMOUNTS OF IRON(III) WITH FERRON*

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INTRODUCTION

The sensitive and selective colour reaction between iron(III) and ferron (7-iodo-8-hydroxyquinoline-5-sulphonic acid) has been studied by many authors[2–9], who applied it to the visual detection and the spectrophotometric determination of iron(III), and as an indicator in the complexometric titration of iron(III). For the qualitative test with ferron, FEIGL[10] stated that only large amounts of intensely coloured ions and strong oxidizing agents interfere.

The "resin spot test", a new type of test proposed by one of the present authors[11–13], has essential merits in the efficient concentration of traces of coloured ions and in the ease with which most interferences by diverse ions of a charge opposite to that of the adsorbed ion are removed. In the present work the resin spot test is applied to the iron(III)–ferron reaction, thus further developing the series of ultramicro tests for iron reported by one of the present authors, *i.e.*, a test for iron(II), with α,α'-dipyridyl[12], and for iron(III) with phenolic reagents, *e.g.*, tiron, 5-sulphosalicylic acid and chromotropic acid[14].

The sulphonic acid group in the reagent is highly dissociated in aqueous media and provides the excellent water-solubility of the chelate. Since the 1 : 3 iron(III)–ferron chelate anion[3] formed has three such groups and is fairly voluminous, it is quite reasonable to presume a high ion-exchange selectivity on strongly basic anion-exchange resins. Moreover, in the visual detection of iron(III), ferron is favored by the sharpness of the colour change from yellow to green on chelation. The present investigation shows that the intense colour which appears on the surface of the resin grains so enhances the sensitivity of the test that even nanogram amounts of iron(III) can readily be detected.

EXPERIMENTAL

Reagents

The chemicals used were of reagent grade unless otherwise specified.

Stock solution of iron(III): This was prepared by dissolution of iron(III) chloride

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in 0.1 *F* hydrochloric acid so as to contain 10.00 ± 0.03 mg of iron(III) per ml; the solution was standardized gravimetrically as Fe_2O_3. A series of standard iron(III) solutions was readily prepared by diluting the stock solution with iron-free 0.01 *F* hydrochloric acid. A solution containing 2.00 p.p.m. iron(III) was used for the study of the optimum conditions for the test.

Stock solutions of other ions: For the purpose of studying the influences of diverse cations, stock solutions of various metals were prepared from nitrates, chlorides or sulphates so as to contain 10 to 50 mg of each cation per ml. To avoid the hydrolysis of metal ions, they were dissolved in dilute acids and in some cases in rather concentrated ones. Stock solutions of anions were prepared from their alkali or ammonium salts.

Aqueous stock solution of ferron: 20 mg of ferron (Wako, Japan) was dissolved in 10 ml of de-ionized water.

Buffer solutions: The buffer solutions (0.1, 0.3 and 1 *F*) were : pH 2.2 and 2.8 (monochloroacetic acid–sodium monochloroacetate), pH 4.4 (acetic acid–sodium acetate) and pH 9.0 (ammonia–ammonium chloride). The solutions were found to be free from any trace of iron. The pH values were determined with pH test papers, which was of sufficient accuracy for the present purpose.

Other reagents: Hydrochloric acid was distilled repeatedly after being treated with a few g of disodium hydrogen phosphate to remove any trace of iron(III). Nitric acid was also distilled.

Ion-exchange resins

Colourless or pale-coloured resins were used. Before use the resins were conditioned as follows. Commercial anion-exchange resins in the chloride form were washed thoroughly with 0.5 *F* hydrochloric acid to remove traces of iron(III) and other metal impurities. The purified resin was converted to the hydroxide form with 2 *F* solution of sodium hydroxide, washed with de-ionized water and again converted to the chloride form with dilute hydrochloric acid. This cycle was repeated once more, and the resin was washed thoroughly with de-ionized water and dried at room temperature. In some cases the hydroxide cycle was replaced by a nitrate cycle. Strongly basic resins (Dowex 1-X1, -X2, -X4, -X10, -X16 and Dowex 2-X2), a moderately strong basic resin (Amberlite XE-114), and a weakly basic resin (Amberlite IR-45), were used in the chloride form.

Dropping capillary pipettes

Capillary pipettes were drawn from a glass tube. One drop of de-ionized water delivered from them was 0.04 ± 0.002 ml.

PROCEDURE

From the results of preliminary experiments the following procedure was adopted to determine the best conditions.

On a white spot plate, mix a few grains of a pale-coloured anion-exchange resin successively with a drop of buffer solution and a drop of aqueous solution of the reagent*. After a few min**, add a drop of the test solution* and observe the dull green

* The above order of mixing is quite essential, since addition of air-dried resin beads in the solution mixture delays the colour development in the resin phase.

** On standing for more than 5 min without adding the test solution the resin beads are coated with an intense yellowish orange colour by the reagent anion, and the greenish colour of the chelate in the resin phase becomes somewhat difficult to observe.

to dark green colour which gradually appears in the resin phase, especially on the "edge" of the grains. Use of a magnifying glass of about 20× is recommended. It is essential to avoid any contamination from dust by covering the spot plate with a glass plate, for the present resin spot test is of extremely high sensitivity.

RESULTS AND DISCUSSION

In order to establish the optimum conditions for the present test, the relative colour intensities on the resin phase and in the outer solution were observed semi-quantitatively[15] under various conditions.

Effects of resin type and their degree of cross-linkage

To follow the relationship of the colouration of the resin phase with the nature of the functional groups and degree of cross-linkage of the resins, a few grains of the resin, 0.1 *F* buffer solution of pH 2.8, and an aqueous 0.05% solution of the reagent were used. The following order of the apparent colour intensities of the resin phase was obtained 30 min after the addition of the reagents: Dowex 1-X1 > -X2 ≃ -X4 ≃ -X10 > Dowex 2-X2 ≫ Dowex 1-X16 ≃ Amberlite XE-114 ≃ Amberlite IR-45. Hence, Dowex 1-X1 was mainly used in the following comparisons.

When the reagent was adsorbed by the resin, the resin phase assumed a "uniform" yellow colour; its intensity increased gradually. The iron(III)–ferron chelate gave the colour most intensely on the "edge" of the resin beads. These results would be explained by the fact that the trivalent chelate anion is much larger than the univalent reagent anion, so that the diffusion of the former within the resin phase would be considerably lower. These phenomena will be studied further in detail and reported elsewhere.

Effect of pH

The effect of the pH of the reaction medium on the colouration in the resin phase was studied with Dowex 1-X1, 0.05% reagent and 0.1 *F* buffer solutions of pH 2.0, 2.8, 4.4 and 9.0. In each case the colours were compared 20 min after the addition of the reagent. In the presence of 80 ng of iron(III) the solution phase was colourless to pale yellow in the pH range of 2.0 to 9.0, and was almost identical with the case when no iron(III) was added. On the other hand the resin phase showed distinct colourations as follows. On the edge of the resin phase was observed a greyish green colour over the pH range 2.0 and 9.0, whereas the centre parts of the particles became pale yellow at pH 2.8 to 9.0 and almost colourless at pH 2.0. If no iron(III) was added, the resin phase showed only a slight pale yellow colour except at pH 4.0 where a dull yellow colour covered the beads. The sensitivities of the present test at various pH values were found to be in the following order: pH 2.8 > pH 4.4 > pH 2.0 ≫ pH 9.0, and the buffer solution pH 2.8 was used in all later work.

The effects of the concentration of the buffer solutions on the colour intensity of the resin phase by the chelate were also studied. The resin species, the pH of the buffer solution and the concentration of the reagent were fixed, and the concentration of the buffer solution was varied from 0.1 to 1.0 *F*. With 1 *F* buffer solution the colour formed on the resin phase by the iron(III)–ferron chelate was a little weaker than that with 0.1 and 0.3 *F* buffers immediately after the addition of the test solution, but no difference was observed after 10 min. The same was true for the acetic acid–sodium acetate system

(pH 4.4). Consequently, the 0.1 *F* buffer solution of pH 2.8 was used for the determination of the optimum conditions. However, when the test solution had been prepared in rather concentrated acid, 1 *F* buffer solution was also used to control the pH of the solution.

Effect of the reagent concentration

Dowex 1-X1 and 0.1 *F* buffer solution of pH 2.8 were used; in each case the colours were compared 20 min after the addition of the reagent. The resin phase assumed a greyish green colour with 0.01 and 0.05% solutions of the reagent and a dull green colour with concentrations of 0.1 and 0.2%. Since the reagent back-ground colour was intense with 0.1 or 0.2% of reagent (*viz.*, dull yellow to dark yellow), 0.01 and 0.05% solutions of the reagent were best for detection of iron(III). When the effects of diverse metal ions which could react with the reagent to form colourless chelates were considered, a 0.05% solution of the reagent was used.

Effect of the salt content of the test solution

Since the ion-exchange selectivity of a simple ion generally decreases with increasing ion concentration in the solution phase, the effects of the total ion concentration on the colouration of the resin phase by the chelate anion were tested by adding a few drops of 1, 2.5 and 5 *F* solutions of sodium chloride along with the test solution. Increasing concentrations of sodium chloride slightly delayed the colour development. In the extreme case when a 5 *F* (saturated) solution of sodium chloride was added, the colour intensity of the resin phase after 10 min was considerably lower than that obtained without sodium chloride. After 20 min, however, the difference in the colour intensity was reduced, and after 50 min no difference was observed. (Similar results were obtained for the colouration of the resin phase by the reagent anion itself). Such tendencies would be explained by a decrease in the swelling of the resin beads caused by the increased outer ion concentration, which would also lower the adsorption velocity of the chelate on the resin phase.

RECOMMENDED PROCEDURE

The above results showed that the resin spot test for iron(III) is most efficiently carried out with a light-coloured strongly basic anion-exchange resin of low cross linkage (*e.g.*, Dowex 1-X1) in the chloride form, along with 0.1 to 1 *F* buffer solution of pH 2.8 and an aqueous 0.05% solution of ferron*.

LIMIT OF IDENTIFICATION

The limit of identification of the test by the recommended procedure was determined. Values of the limits of identification for iron(III) in nanogram with various resins determined after standing for 10–20 min or for 50 min are shown respectively in parentheses as follows:

Dowex 1-X1 (4, 2); -X2 (4,2); -X4 (4, 2); -X10 (4, 4); Dowex 2-X2 (8, 8); Amberlite XE-114 (80, 40) and Amberlite IR-45 (400, 200). The corresponding values by

* When the temperature falls below 10°, the colour development in the resin phase by chelate up-take is rather delayed. In this case, the spot plate containing the mixture is warmed gently on a water bath to promote the reaction.

the usual spot test without addition of resin beads were found to be only 200 ng of iron(III) in both cases. Dowex 1-X1, -X2 and -X4 gave the best results, *viz.*, the limit of identification after 10 to 20 min was 4 ng per 0.04 ml of the test solution ($1:1\cdot10^7$) and that after 50 min 2 ng ($1:2\cdot10^7$). When a drop of 5 *F* sodium chloride solution was added to a drop of the sample solution, the colouration was somewhat delayed in the first 10 min, but the limits of identification after 20 or 50 min were practically equal to those obtained without adding the salt, and the present resin spot test was proved to be 50–100 times as sensitive as the usual spot test.

INFLUENCES OF FOREIGN SUBSTANCES

The influences of various compounds on the present test were exhaustively surveyed. The results are listed in Table I. Cobalt(II), copper(II), chromium(VI), uranium(VI) and vanadium(V) interfered (see the remarks in the table).

TABLE I

INFLUENCE OF FOREIGN COMPOUNDS ON THE DETECTION OF IRON(III) WITH FERRON BY THE RESIN SPOT TEST

Foreign ion	*Added salt*	*Colour of the resin phase*[a]	*Amount of foreign substance (μg)*	*Amount of detectable iron(III) (μg)*	*Limiting proportion*	*Remarks*
Mg(II)	$MgCl_2$	pl Ye to Ye	400	0.008	$1:5\cdot10^4$	
Ca(II)	$CaCl_2$	pl Ye to Ye	1600	0.008	$1:2\cdot10^5$	
Sr(II)	$SrCl_2$	pl Ye to Ye	2000	0.008	$1:2.5\cdot10^5$	
Ba(II)	$BaCl_2$	pl Ye to Ye	4000	0.008	$1:5\cdot10^5$	
Ti(IV)	$TiOSO_4$	dk Ye(edge), lm Ye(centre)	0.21	0.013	$1:1.6\cdot10$	
		lm Ye	63	0.02	$1:3.2\cdot10^3$	b
V(V)	NH_4VO_3	dk Grn to dl Grn	0.8	0.2	1:4	c
		cl to sl dk Ye	1.6	0.02	$1:8\cdot10$	b
Cr(III)	$KCr(SO_4)_2$	lt Ol	13	0.008	$1:1.6\cdot10^3$	c
		wk dk Ye	54	0.013	$1:4\cdot10^3$	i
Cr(VI)	K_2CrO_4	lt Br to dkOr	1.1	0.013	$1:8.5\cdot10$	
Mo(VI)	Na_2MoO_4	dk Or	4.3	0.013	$1:3.3\cdot10^2$	
W(VI)	Na_2WO_4	wk lm Ye	14	0.008	$1:1.8\cdot10^3$	
U(VI)	$UO_2(OAc)_2$	dk Ye Or to dk Or	1.1	0.013	$1:8.5\cdot10$	
Mn(II)	$MnSO_4$	pl Ye to dl Ye	1400	0.008	$1:1.8\cdot10^5$	
Co(II)	$CoCl_2$	dk Ye Or to dk Or	0.13	0.008	$1:1.6\cdot10$	
Ni(II)	$NiCl_2$	wk Ye Grn to cl	1600	0.016	$1:1\cdot10^5$	c,f
Cu(II)	$CuSO_4$	lt Ol	0.4	0.02	$1:2\cdot10$	c
		wk dk Ye	54	0.013	$1:4\cdot10^3$	d
Zn(II)	$ZnSO_4$	pl Ye	140	0.008	$1:1.8\cdot10^4$	
Cd(II)	$Cd(NO_3)_2$	pl Ye	1300	0.013	$1:1\cdot10^5$	g
Hg(II)	$HgCl_2$	sl br lm Ye	1100	0.008	$1:1.4\cdot10^5$	
Al(III)	$KAl(SO_4)_2$	pl Ye	64	0.008	$1:8\cdot10^3$	
Ge(IV)	GeO_2	wk dl Ye	19	0.013	$1:1.5\cdot10^3$	g
Sn(IV)	$SnCl_4$	cl to wk lm Ye	26	0.013	$1:2\cdot10^3$	h
		cl to wk lm Ye	260	0.013	$1:2\cdot10^4$	b
Pb(II)	$Pb(NO_3)_2$	pl Ye	1600	0.008	$1:2\cdot10^5$	
Sb(III)	$SbCl_3$	cl to pl Ye	6.4	0.008	$1:8\cdot10^2$	
Bi(III)	$Bi(NO_3)_3$	cl to sl pl Ye	64	0.008	$1:8\cdot10^3$	h
		pl Ye to wk lm Ye	130	0.027	$1:5\cdot10^3$	b

TABLE I (continued)

Foreign ion	*Added salt*	*Colour of the resin phase*[a]	*Amount of foreign substance (μg)*	*Amount of detectable iron(III) (μg)*	*Limiting proportion*	*Remarks*
F^-	KF	pl Ye	26	0.013	$1:2\cdot10^3$	
Br^-	KBr	pl Ye	7200	0.004	$1:1.8\cdot10^6$	
I^-	KI	pl Ye to Re	64	0.008	$1:8\cdot10^3$	
SCN^-	KSCN	pl Ye	6400	0.008	$1:8\cdot10^5$	
NO_3^-	KNO_3	pl Ye	1600	0.008	$1:2\cdot10^5$	
NO_2^-	$NaNO_2$	lm Ye to ltOl	5.4	0.013	$1:4.2\cdot10^2$	
		pl Ye	2600	0.013	$1:2\cdot10^5$	e
SO_4^{-2}	K_2SO_4	pl Ye	960	0.008	$1:1.2\cdot10^5$	
HPO_4^{-2}	Na_2HPO_4	pl Ye	1300	0.008	$1:1.6\cdot10^5$	
$B_4O_7^{-2}$	$Na_2B_4O_7$	wk lm Ye	800	0.008	$1:1\cdot10^5$	
$S_2O_3^{-2}$	$Na_2S_2O_3$	pl Ye	540	0.013	$1:4.2\cdot10^4$	
$HCOO^-$	HCOONa	pl Ye	1600	0.008	$1:2\cdot10^5$	
$C_2O_4^{-2}$	$(NH_4)_2C_2O_4$	pl Ye	16	0.008	$1:2\cdot10^3$	
$C_4H_4O_6^{-2}$	Rochelle salt	pl Ye	1600	0.008	$1:2\cdot10^5$	
$C_6H_5O_7^-$	Ammonium citrate	pl Ye	1600	0.008	$1:2\cdot10^5$	
EDTA	Disodium salt	dl Ye	1.9	0.02	$1:9.5\cdot10$	
H_2O_2	——	wk dk Ye	600	0.02	$1:3\cdot10^4$	

a The colouration of the resin phase by foreign compound itself. Colour code[11,16]: sl, slightly; wk, weakly; cl, colourless; dk, dark; pl, pale; dl, dull; lm, lemon; lt, light; Br, brown; br, brownish; Grn, green; Ol, olive; Or, orange; Re, red; Ye, yellow.
b After 3 drops of a 5% solution of ammonium citrate were added, a few grains of resins were placed in the test solution.
c These values were obtained only by running a blank test in parallel.
d After 3 drops of a saturated aqueous solution of thiourea were added, the test was carried out.
e The test was carried out after the sample solution was evaporated to dryness on a water bath with a drop of 3 *F* hydrochloric acid.
f If the colour of the iron(III)–ferron chelate on the resin phase is obscured by that of the foreign compound in the outer solution, it is advisable to observe the resin beads after soaking off the outer solution and washing the beads with a few drops of de-ionized water.
g 3 drops of a 0.05% solution of ferron were used.
h 2 drops of a 0.05% solution of ferron were used.
i After 3 drops of a 0.05% aqueous solution of ethylenediamine were added, the test was carried out.

SUMMARY

A new ultramicro method for detection of iron(III) is described. A colourless, strongly basic anion-exchange resin of low cross-linkage in the chloride form is used to enhance the sensitivity of the colour reaction of iron(III) with ferron. The limit of identification of the new "resin spot test" is 4 ng of iron(III) ($1:1\cdot10^7$) after 10 to 20 min and 2 ng ($1:2\cdot10^7$) after 50 min. The test is 50–100 times as sensitive as the usual spot test. Serious interferences were observed with cobalt(II), copper(II), chromium(VI), uranium(VI) and vanadium(V); the elimination of their interferences was also studied.

RÉSUMÉ

Une nouvelle méthode ultramicrochimique est décrite pour l'identification du fer(III). Une résine d'échange d'ions est utilisée pour augmenter la sensibilité de la coloration obtenue avec le ferron. On peut ainsi déceler jusqu'à 2 nanogrammes de fer; sensibilité environ 100 fois supérieure à celle obtenue avec les réactions à la touche usuelles. Cobalt(II), cuivre(II), chrome(VI), uranium(VI) et vanadium(V) gènent.

ZUSAMMENFASSUNG

Beschreibung einer neuen ultramikrochemischen Methode zum Nachweis von Eisen(III). Sie beruht auf der Reaktion mit Ferron, wobei jedoch durch Zusatz eines Anionenaustauschers eine Farbintensivierung erreicht wird. Erfassungsgrenze: 2 Nanogramm. Kobalt, Kupfer, Chrom(VI), Uran(VI) und Vanadium(V) stören.

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ÜBER DIE GEWICHTSANALYTISCHE ZIRKONBESTIMMUNG IN ZIRKONKONZENTRATEN

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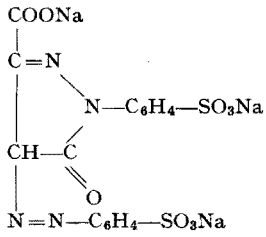
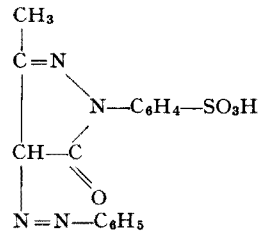
Durch seine zahlreichen Anwendungen sowohl als Element wie auch in verschiedenen Verbindungen[1] ist Zirkon heute ein technisch besonders wichtiges Metall. Aus diesem Grund bietet seine Bestimmung in Zirkonkonzentraten ein wichtiges theoretisches und praktisches Problem.

Unter den in der Literatur beschriebenen gewichtsanalytischen Methoden is die der Fällung mit Mandelsäure[2] ausgezeichnet durch ihre Selektivität und hat sich durch die genauesten Ergebnisse bei der gravimetrischen Zirkon(IV)-bestimmung als die Beste bewährt. Wie Verfasser hinweist, kann man mit Mandelsäure befriedigend 50–300 mg ZrO_2 bestimmen. Die Ergebnisse werden jedoch ungenau bei Proben mit einem niedrigeren Zirkongehalt. Bei Anwesenheit von verschiedenen, häufig vorhandenen Kationen is ein Fehler von $\pm$ 0.2–0.5 mg für 110 mg ZrO_2 angegeben.

Kürzlich wurden zwei neue Methoden beschrieben die als Fällungsreagenzien zwei Derivate der Pyrazolonfarbstoffe verwenden und zwar das Tartrazin[3] und das Flavazin L (freie Säure).[4]



Tartrazin



Flavazin L

Beide Methoden zeichnen sich durch Empfindlichkeit, Selektivität und Geschwindigkeit aus. Es wurde daher untersucht, ob sie sich zur Bestimmung des Zirkons in den Auszügen der Zirkonkonzentrate eignen. In der vorliegenden Arbeit werden beschrieben:

A. Die optimalen Bedingungen für den Aufschluss der Zirkonkonzentrate.

B. Die Arbeitweise für die Bestimmung des Zirkons.

C. Der Vergleich zwischen den neu vorgeschlagenen Methoden und der Fällung mit Mandelsäure.

A. Optimale Bedingungen für den Aufschluss der Zirkonkonzentrate

Um die optimalen Bedingungen für den Aufschluss fest-zu-stellen, wurden die in der Literatur als die besten vorgeschlagenen Verfahren einer kritischen Prüfung unterzogen.

Aufschluss durch Schmelzen mit alkalischen Agenzien (NaOH, Na_2O_2, Na_2CO_3, $NaKCO_3$, $Na_4B_4O_7$) oder mit $K_2S_2O_7$. Diese Aufschlüsse sind meistens unvollständig. Die Manipulationen sind manchmal schwierig (Na_2O_2) und in anderen Fällen ist die erforderliche Temperatur sehr hoch (1000°–1200°) ($Na_4B_4O_7$).[4]

Aufschluss mit Borax nach Entfernung der Kieselsäure, zwecks Ausschaltung der Zirkonadsorption[5]. Die Kieselsäure wird mit HF + H_2SO_4 entfernt und der Rückstand mit Borax geschmolzen. Auch in diesem Falle ist der Aufschluss nicht vollständig und die gänzliche Vertreibung der Schwefelsäure langwierig.

Die Anwesenheit grösserer Mengen von Fremd-Ionen (besonders Fe^{+3}) im Auszug mit 6 *N* Salzsäure erschwert die Anwendung dieses Verfahrens zur Bestimmung des Zirkons in Zirkonkonzentraten.

Bei dem Verfahren nach VALCHA[6] wird die Kieselsäure mit HF + H_2SO_4 abgeraucht, ohne jedoch die Schwefelsäure vollständig zu entfernen. (Der Rückstand muss feucht bleiben). Nach Kochen des Rückstandes mit HCl (1 : 5) und H_2O_2 wird filtriert, der Rückstand mit einem Gemisch von Na_2CO_3 und Borax (4 : 1) geschmolzen und die erkaltete Schmelze in 6 *N* Salzsäure gelöst.

Durch dieses Verfahren wird der Zeitaufwand bedeutend verringert, ein vollständige Aufschluss erreicht und die fremden Kationen gröstenteils in dem ersten salzsauren Auszug abgetrennt. Dies erlaubt eine leichte Bestimmung des Zirkons.

B. Arbeitsvorschrift

Aufschluss

0.5–1 g Zirkonkonzentrat werden in einem Achatmörser feinst zerrieben in einem Platintiegel mit 5 ml H_2SO_4 (1 : 1) und 10 ml HF versetzt und von Zeit zu Zeit mit einem Platinspatel innig gemischt. Um Verluste an ZrF_4 zu vermeiden, wird vorsichtig verdampft bis zu reichlichem Auftreten von SO_3-Dämpfen.

Zur sicheren Entfernung der SiO_2 wiederholt man nochmals die Behandlung mit 2–3 ml HF; die Schwefelsäure wird von neuem fast bis zur Trockne vertrieben. Der Rückstand, der noch feucht sein muss, wird mit 50–60 ml verdünnter HCl (1 : 5) aufgenommen und zur vollständigen Oxidation des Eisens mit einigen Tropfen H_2O_2 versetzt. In dieser Lösung gibt man Filterbrei und kocht 5–10 Min. (Fein geschnittenes Aschefreies Filterpapier wird in verdünnter Salzsäure erwärmt, der Brei filtriert und bis zur neutralen Reaktion mit heissem Wasser gewaschen).

Man filtriert durch ein dichtes Filterpapier (Blauband) und wäscht gründlich mit verdünnter, heisser, Salzsäure (1 : 99) bis das Filtrat farblos abläuft. Das Filtrierpapier wird samt Niederschlag vorsichtig in dem schon vorher benutzten Platintiegel verascht und auf Rotglut erhitzt. Der Glüh-rückstand wird mit einem Gemisch von Na_2CO_3 und Borax (1 : 4) in Überschuss (5 : 1) am Gebläse geschmolzen wobei man die Temperatur allmählich steigert; die erhaltene durchsichtige, glasige Schmelze, bleibt noch 20–30 Sek über der vollen Flamme. Der Aufschluss ist beendet wenn die Schmelze vollkommen durchsichtig geworden ist. Nach dem Erkalten wird mit heissem Wasser ausgezogen, durch ein dichtes Filtrierpapier (Blauband) filtriert, einige mal mit heisser 5%-iges Natronlauge und schliesslich zweimal mit heissem

Wasser gewaschen. Der Rückstand, der das Zirkon als Karbonat enthält, wird in heisser 6 *N* Salzsäure gelöst. Man ergänzt die Lösung in einem 100-ml Messkolben mit Wasser bis zur Marke und entnimmt sofort die Proben für die Analyse.

Bestimmung mit Tartrazin

Ein Teil (oder der ganze Auszug) wird auf 60–80° erhitzt und auf ein pH von 0.5–1 (orange Farbe des Cresolrots) eingestellt. Dann wird tropfenweise 1% wässeriger Tartrazinlösung bis zu vollständigen Ausfällung zugegeben. Der reichlich gebildete, gelbe Niederschlag setzt sich unmittelbar ab. Der Niederschlag wird mit heissem Wasser auf ein Filter (Blauband) gebracht und so lange ausgewaschen bis das ablaufende Filtrat nur noch schwach gelb gefärbt ist. Das Filter mit dem Niederschlag wird in einen Porzellan-, Quarz- oder Platintiegel gebracht, mit kleiner Flamme getrocknet, dann verascht und zum Schluss im elektrischen Ofen bei 1100° bis zu konstantem Gewicht geglüht.

Bestimmung mit Flavazin

Die Arbeitsweise ist ähnlich wie bei Tartrazin. Die Fällung wird aber bei Zimmertemperatur mit einer 0.5% wässerigen Flavazinlösung L (freie Säure) ausgeführt. Nach Absetzen des gelben, kristallinischen Niederschlags wird durch ein mitteldichtes Filter filtriert (Weissband) und mit kaltem Wasser gewaschen.

Die Ergebnisse der Bestimmungen mit Tartrazin und Flavazin sind in den Tabellen I und II zusammengefasst. Wie daraus zu ersehen ist, werden mit Tartrazin und Flavazin L unter den festgestellten Bedingungen die zugesetzten Mengen einer Zirkon-Standardlösung zu einem Zirkonkonzentrat wieder gefunden. Die Abweichung zwischen der zugesetzten und gefundenen Menge Zirkon beträgt höchstens 0.3 mg.

TABELLE I

BESTIMMUNG MIT TARTRAZIN

Art der Probe	*Konzentrat* g	*Zr Ausgangswert* g	*Zr zugegeben* g	*Zr gefunden* g	*Abweichung* g
Konzentrat A	0.1000	0.0167	—	—	—
	0.1000	0.0244	0.0076	0.0077	+ 0.0001
Konzentrat B	0.01000	0.0158	—	—	—
	0.01000	0.0210	0.0052	0.0052	—
Konzentrat C	0.4000	0.0059	—	—	—
	0.4000	0.0138	0.0076	0.0079	+ 0.0003
Konzentrat D	0.4000	0.0213	—	—	—
	0.4000	0.0296	0.0083	0.0083	—
Konzentrat E	0.4000	0.0175	—	—	—
	0.4000	0.0250	0.0074	0.0075	+ 0.0001
Konzentrat F	0.4000	0.0135	—	—	—
	0.4000	0.0209	0.0074	0.0074	—

Die Ergebnisse der Bestimmungen mit Tartrazin und Flavazin bei verschiedenen Mengen desselben Auszugs sind in den Tabellen III und IV wiedergegeben. Aus diesen Tabellen folgt, dass die Ergebnisse reproduzierbar sind. Die Abweichung beträgt höchstens 0.18%.

TABELLE II

BESTIMMUNG MIT FLAVAZIN L

Art der Probe	*Konzentrat g*	*Zr Ausgangswert g*	*Zr zugegeben g*	*Zr gefunden g*	*Abweichung g*
Konzentrat A	0.1000	0.0167	—	—	—
	0.1000	0.0243	0.0076	0.0076	—
Konzentrat B	0.1000	0.0157	—	—	—
	0.1000	0.0209	0.0052	0.0052	—
Konzentrat C	0.4000	0.0058	—	—	—
	0.4000	0.0137	0.0078	0.0079	+ 0.0001
Konzentrat D	0.4000	0.0215	—	—	—
	0.4000	0.0298	0.0083	0.0083	—
Konzentrat E	0.4000	0.0175	—	—	—
	0.4000	0.0249	0.0074	0.0074	—
Konzentrat F	0.4000	0.0135	—	—	—
	0.4000	0.0208	0.0074	0.0073	— 0.0001

TABELLE III

BESTIMMUNG MIT TARTRAZIN

Art der Probe	*Konzentrat g*	*Zr g*	*Zr % g*	*Abweichung % g*
Konzentrat A	0.1000	0.0167	16.70	—
	0.2500	0.0417	16.68	0.02
Konzentrat B	0.1000	0.0158	15.80	0.08
	0.2500	0.0397	15.88	
Konzentrat C	0.4000	0.0059	1.46	0.02
	3	0.0438	1.46	
Konzentrat D	0.4000	0.0213	5.33	0.03
	1	0.0536	5.36	

TABELLE IV

BESTIMMUNG MIT FLAVAZIN L

Art der Probe	*Konzentrat g*	*Zr g*	*Zr % g*	*Abweichung % g*
Konzentrat A	0.1000	0.0167	16.70	0.02
	0.2500	0.0417	16.68	
Konzentrat B	0.1000	0.0157	15.70	0.18
	0.2500	0.0397	15.88	
Konzentrat C	0.4000	0.0058	1.45	0.01
	3	0.0438	1.46	
Konzentrat D	0.4000	0.0215	5.38	0.01
	1	0.0537	5.37	

C. Vergleich zwischen den neu vorgeschlagenen Methoden und jener Mandelsäure

Um die mit Tartrazin und Flavazin L erhaltenen Ergebnisse mit der Mandelsäuremethode zu vergleichen, wurden Bestimmungen in der gleichen sowie in verschiedenen Ausgangslösungen (Konzentrate A und B bzw. C und D) mit den drei Reagenzien durchgeführt. Wie aus Tabelle V zu ersehen ist, wurde hierbei eine befriedigende

Übereinstimmung erzielt. Die grösste Abweichung zwischen den Bestimmungen mit Tartrazin, Flavazin und Mandelsäure beträgt 0.5 mg, wobei die Werte mit Mandelsäure durchwegs etwas tiefer liegen als die Tartrazin und Flavazinwerte.

TABELLE V

VERGLEICH ZWISCHEN DEN DREI METHODEN

Art der Probe	*Konzentrat* g	*Zr Tartrazin* g	*Zr Flavazin L* g	*Zr Mandelsäure* g
A	0.25	0.0417	0.0417	0.0414
B	0.25	0.0397	0.0397	0.0394
C	3	0.0438	0.0438	0.0433
D	1	0.0536	0.0537	0.0534

Die Fällungen mit Tartrazin und Flavazin L setzen sich rasch ab und können sofort filtriert werden. Die mit Mandelsäure entstandene Fällung muss 15–30 Min auf dem Wasserbad erwärmt werden und muss vor der Filtration mindestens 2 Stunden stehen. Die kleinste mit Mandelsäure bestimmbare Zirkonmenge beträgt 0.05 g ZrO_2, während man mit Tartrazin und Flavazin L noch 0.01 g ZrO_2 erfassen kann. Diese neuen Methoden können daher auch für ärmere Zirkonkonzentrate benutzt werden.

ZUSAMMENFASSUNG

Nach Aufschluss der Probe nach einem modifiziertem Verfahren, werden zwei neue Reagenzien — Tartrazin und Flavazin L (freie Säure) — für die gewichtsanalytische Bestimmung des Zirkons (IV) in Zirkonkonzentraten vorgeschlagen. Die Vorzüge der Anwendung von Tartrazin und Flavazin L gegenüber jener von Mandelsäure sind: die Niederschläge setzen sich rasch ab und können sofort filtriert werden. Wegen ihrer grösseren Empfindlichkeit, können beide Reagenzien für die Bestimmung des Zirkons in Zirkonarmen Konzentraten angewandt werden.

SUMMARY

A new gravimetric method involving tartrazine or flavazine L as reagent has been developed for the rapid determination of zirconium in zirconiferous concentrates. The methods are compared with the mandelic acid method and advantages are outlined.

RÉSUMÉ

On propose un procédé pour le dosage gravimétrique, rapide et direct du zirconium dans des concentrés zirconifères, en utilisant deux nouveaux réactifs: tartrazine et flavazine L. Les éléments présents ne gènent pas.

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MECHANICAL FEED BURNER WITH TOTAL CONSUMPTION FOR FLAME PHOTOMETRY AND ATOMIC ABSORPTION SPECTROSCOPY

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INTRODUCTION

Two types of burners have principally been used in the past for flame photometry and atomic absorption spectroscopy. These burners are the total consumption burner and Lundegarde type burner; each has limitations. With a total consumption type burner (aspiration), the feed rate of the sample is dependent on physical characteristics of the solution such as viscosity, surface tension, etc. It is also subject to clogging

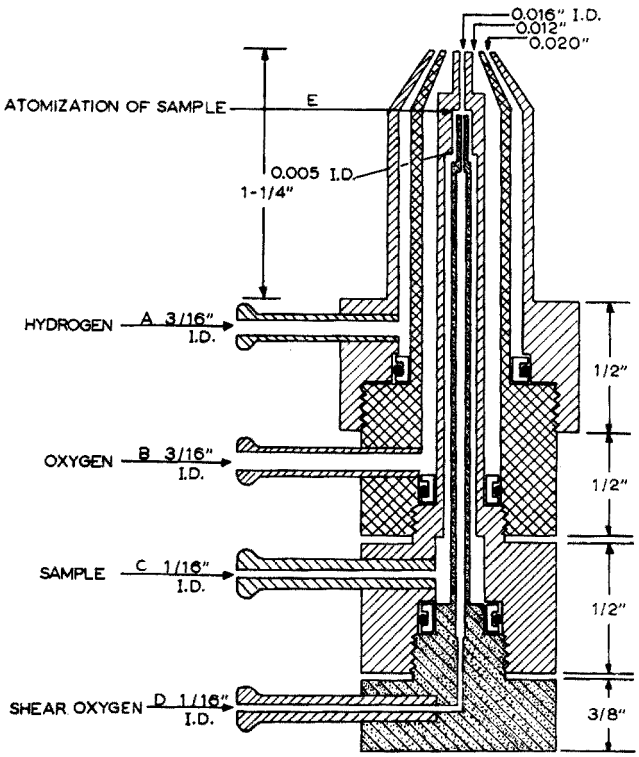

Fig. 1. Diagram of mechanically fed burner.

by small particles included in the sample. With the second type burner little control is available over the feed rate. Further there is the possibility that the sample will fractionate and that the portion swept into the burner may not be representative of the solution from which it came.

To alleviate these problems, a forced feed burner has been designed. This burner is capable of maintaining a steady feed rate of 4 ml or less per min with total consumption of the sample. The burner is illustrated in Fig. 1.

BURNER FABRICATION

Construction of this burner must be carried out with a high degree of precision. For satisfactory performance, the components must be of the correct dimensions and be properly adjusted. The most critical and difficult adjustment is the alignment of the high pressure oxygen capillary and the sample exit capillary at point E. It is important that these tubes be carefully adjusted to give maximum nebulization of the sample. This was achieved by trial and error. However, it is felt that the use of lateral adjusting screws through the sides of the burner would enable these capillaries to be made concentric *in situ*.

Adjustments of the other components of the burner are less critical. These can be achieved fairly easily, providing the components are concentric and of the correct dimensions.

PRINCIPLE

Oxygen and hydrogen are fed at suitable rates to points A and B of the burner. These form the main constituents of the flame. Their feed rates are controlled by pressure regulation in the normal fashion. A second source of oxygen enters the burner at point D and is controlled independently. This oxygen is under high pressure (approximately 150 lbs./sq. in.). Its flow rate is fast, but the volume used is low because of the small diameter of the capillary. A liquid sample is mechanically fed at point C and comes into contact with the high velocity oxygen at point E. At this point the oxygen exercises a shearing force on the liquid solution. This causes the formation of very fine droplets of sample. A mixture of droplets and oxygen are then swept into the base of the flame where combustion or decomposition of the sample takes place in the normal fashion.

A burner for flame photometry carries out two functions; *i.e.*, it breaks down the sample to a fine spray and then allows interaction between the spray and the flame. It has been found that the intensity of flame spectra is controlled considerably by the efficiency of the burner in atomizing the sample[1]. It is therefore an advantage if the burner atomizes the sample as effectively as possible before introduction into the flame. In the aspiration burner this is accomplished by fragmentation of the sample at the point of introduction to the flame. In the burner described, the high shearing action of the oxygen on the sample is designed to ensure effective atomization. An added advantage of the system is that the sample feed rate and atomization are controlled independently by the mechanical feed system and the shearing oxygen, respectively. This allows the sample feed rate to be maintained constant, even though the fuel–oxygen ratio of the flame is varied over a wide range. This is in direct contrast to the aspiration burner where changes in fuel or oxygen flow to the flame directly affect both the feed rate and the atomization of the sample. Emission

and absorption signals are modified by both the feed rate and the efficiency of atomization and these parameters are dependent on each other. Theoretical interpretation of results is therefore difficult when an aspiration burner is used. However, with a forced feed system, these conditions may be varied independently and the results interpreted more easily.

MECHANICAL FEED SYSTEM

The mechanical feed system used was based on piston displacement of the sample (Fig. 2). This was preferred over a constant pressure feed system because it ensured a constant feed rate, independent of the viscosity of the sample or partial plugging of the feed line.

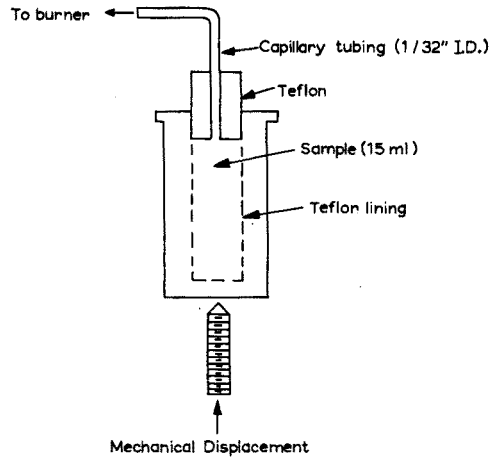

Fig. 2. Mechanical feed system. "Aminco" force feed system, American Instrument Co.

A stoichiometric O_2/H_2 mixture was obtained at pressure 8/2 p.s.i., respectively. The composition of other mixtures of O_2/H_2 bears a similar relation to the pressure. It was concluded that the optimum flame conditions for this burner are as seen in Table I.

TABLE I

Solution	*Fuel pressure (lbs./sq. in.)*			
	Atomic absorption		*Emission*	
	H_2	O_2	H_2	O_2[a]
Aqueous	2.0	0.6	3.5	8.0
Organic	0.2	0.6	0.2	2.0

[a] There is an optimum O_2 pressure for each H_2 setting.

These results indicate the wide variation in conditions required for operation with aqueous or organic solutions. They also show significant differences in optimum conditions when the burner is being used for atomic absorption spectroscopy or flame photometry. It is probable that this relationship between flame conditions and

optimum emission or atomic absorption signal also pertains to commercial aspiration burners.

Teflon lining was used on the equipment because metal linings were subject to acid attack and to plating out of metals from the sample. This can be prevented in the burner by coating with palladium.

Glass syringes are undesirable because of leaks around the piston, and because of piston jamming followed by fracture of the glass syringe due to the mechanical pressure.

PERFORMANCE

As indicated above, the forced feed burner may be capable of handling high sample feed rates. The relation between feed rate and signal was therefore determined. The results for aqueous and organic solvents are shown in Fig. 3. A similar relationship was obtained with the emission signal and sample feed rate. Using a solution of nickel (1 p.p.m.) in acetone, a limit of detection of 0.2 p.p.m. was found for nickel. This is an improvement over commercial aspiration burners used on the same instrumentation for which a detection limit of 1 p.p.m. was found.

It can be seen that the emission signal and absorption signal increase as the feed rate increases to 4 ml/min and does not reach a maximum. Tests were not carried out at feed rates greater than this because the mechanical feeding device was not capable of faster feed rates. It could be anticipated, however, that higher signals would be obtained if the feed rate were increased further. An aqueous sample feed rate of about 0.6 ml/min is typical for an aspiration burner.

Optimum flame conditions

For convenience, a feed rate of 2 ml/min was used in all cases. Solutions of nickel in 2% hydrochloric acid and nickel naphthanate in acetone were used as test samples. The oxygen and hydrogen content of the flame was varied.

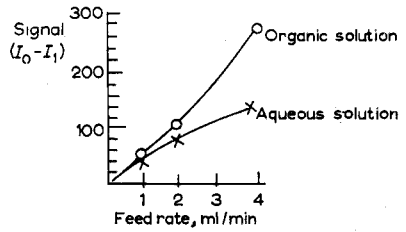

Fig. 3. Absorption signal *vs.* sample feed rate, aqueous and organic solutions. $\lambda = 3414$ Å. Solution: Ni (50 p.p.m.) in (*a*) 2% HCl solution, (*b*) acetone.

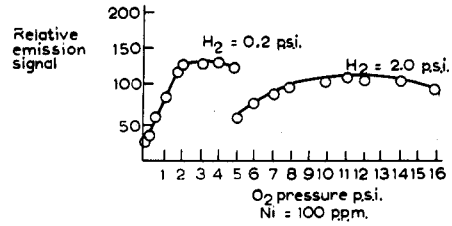

Fig. 4. Optimum flame conditions for emission. Organic solvent (acetone), feed rate: 2 ml/min.

At each different mixture of oxygen and hydrogen, the flame was profiled in order to measure the most intense emission and absorption signal. This was necessary because the most intense signal was generated at varying heights above the base of the flame when the flame composition was varied.

A typical curve showing the relationship between signal (emission or absorption) and flame composition is shown in Fig. 4.

As the pressure of the shear oxygen was increased, the emission and absorption signal increased steadily until a pressure of 150 p.s.i. was reached. At pressures greater than 200 p.s.i., the flame became turbulent, presumably because of turbulence in the oxygen flow. All tests were therefore made at a shear oxygen pressure of 150 p.s.i.

Effect of viscosity

Tests were made on different organic solutions each containing nickel naphthanate to the extent of 10 p.p.m. The results are shown in Table II. Similar tests were made on the emission signal from the same solutions.

TABLE II

EMISSION AND ABSORPTION OF NICKEL IN VARIOUS SOLUTIONS

Nickel concentration = 10 p.p.m. Feed rate: (*a*) Forced feed burner, 1 ml/min; (*b*) Aspiration burner, various (results corrected to 1 ml/min)

Solvent	*Burner type*				*Viscosity at 20°* ($1000\ \eta$)
	Forced feed		*Aspiration burner Absorption* ($I_0 - I_1$)		
	Absorption $I_0 - I_1$	*Emission* E	*Observed*	*Corrected for feed rate*	
Acetone	14.5	33	15	7.0	3.3
n-Heptane	15.5	40	—	—	4.2
Ethyl acetate	13	37	12	7.5	4.5
Methyl alcohol	15	29	9	5.8	5.9
Benzene	16	42	2	1.9	6.5
Toluene	15	38	16	15.5	7.7
Methylcyclohexane	16	39	20	14.0	7.7
Amyl acetate	13.5	36			8.0
Cyclohexane	15.0	35	8	7.3	9.3
Carbon tetrachloride	8	5	5	4.0	9.6
Ethyl alcohol	15	31	6	3.7	12.0
Nitrobenzene	13.5	34	2	1.0	19.8
Isopropanol	15	33			22.5
Varsol	14.5	30	5	9.3	
Water	4	4	3	3.0	10.0

As can be seen, the absorption signal from all the solvents were very similar when the forced feed burner was used. This was most encouraging since it has previously been observed that atomic absorption spectroscopy enjoys a high degree of freedom from interference from other metals present but suffers from interference by variations of the organic solvent in which the sample is tested. However, using the forced feed burner, this source of interference is virtually eliminated, provided, of course, that the viscosity is kept below a certain limiting value.

These experiments on atomic absorption signals indicated that variations due to viscosity were greatly decreased by the efficient atomization of the sample. However, some variation in emission intensity was still apparent. This may be explained by the fact that emission spectra are generated by excited atoms, but the degree of absorption is controlled by the number of unexcited atoms present. It is possible that the total population of metal atoms produced in the flame remains constant even with

different organic solvents. Hence, the absorption signal would be constant and largely independent of the solvent used. However, the number of excited atoms in that population may vary considerably causing variation in emission signal. No measurable effect would be noted on the absorption signal since the number of excited atoms is a small fraction of the unexcited atoms (10^{-6}) and the slight variation in the population of unexcited atoms would be relatively insignificant.

Flame profile of emission and absorption signals

The intensity of emission and absorption signals was measured from different parts of the flame. This was done by masking the flame and collimating the light path so that light from a known portion of the flame entered the monochrometer. The results are shown in Fig. 5. It can be seen that the intensity of the emission from the flame alone reached a maximum at the top of the inner cone. The emission from the nickel reached a maximum just above the tip of the inner cone and then diminished to zero. The intensity of the nickel continuum in the immediate vicinity reached a similar maximum to the 3414 Å line indicating that the line spectra and the background continuum spectra of the nickel probably originated from the same process.

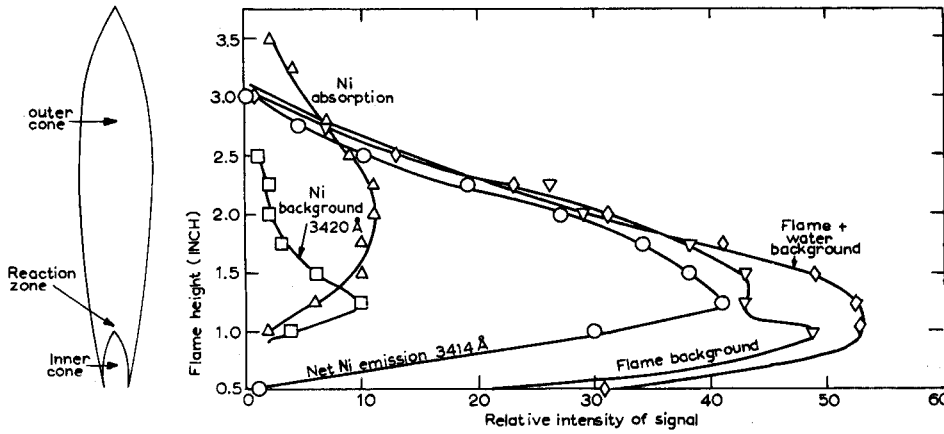

Fig. 5. $NiCl_2$ in ethanol (10 p.p.m. Ni), O_2 = 3.75 p.s.i.; H_2 = 0.2 p.s.i. △ Ni absorption 3414 Å; ◇ flame emission 3414 Å; ▽ flame + water emission 3414 Å; ○ net Ni emission 3414 Å; □ net Ni emission 3420 Å.

It can be seen that the absorption signal reached a maximum at a higher position in the flame. This is probably because the atoms in the ground state have a longer life-time than atoms in excited state. Therefore, some accumulation of atoms in the ground state occurs. It would, therefore, not be expected that the maximum absorption and emission signals would be given in the same part of the flame. This also suggests that excited and unexcited atoms are not in thermal equilibrium.

CONCLUSIONS

The results obtained indicate that this mechanically fed burner operated satisfactorily under test conditions which enable feed rates to be altered independently of oxygen

and fuel rates. Further, much of the interference caused by the use of different organic solvents in atomic absorption spectroscopy was eliminated.

A very desirable feature is that the ratio of fuel and oxygen (or air) can be varied over a very wide range without affecting the atomization and rate of introduction of the sample. Further, by varying the flow rate of the shearing oxygen, the atomization of the sample can be varied independently of other conditions. It is possible to change flame conditions and conditions of introduction of sample independently and over a wide range. This should facilitate flame studies and combustion studies as well as flame photometric and atomic absorption studies. Preliminary studies show that the optimum fuel/oxygen ratio is quite different for aqueous and organic solvents. There is also a change in optimum conditions when the burner is used for atomic absorption instead of flame photometry. Examination of flame profiles also shows that the best flame region for atomic absorption is not the same part of the flame from which the most intense emission spectra emanate.

ACKNOWLEDGEMENTS

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SUMMARY

A mechanical feed burner has been developed for use in flame photometry and atomic absorption spectroscopy. The optimum flame conditions for emission and absorption are very different. These conditions are also modified when organic instead of aqueous solvents are used. When different organic solvents are used, the interference is eliminated with atomic absorption but not emission. Flame profiles of atomic absorption and emission signals indicate that the processes are independent; the best signal for each is obtained at different parts of the flame. With emission, it appears that line spectra and background emission originate from the same process *e.g.* chemiluminescence.

RÉSUMÉ

Description d'un dispositif pour l'introduction mécanique des solutions dans le brûleur pour la photométrie de flamme et la spectroscopie par absorption.

ZUSAMMENFASSUNG

Beschreibung einer Einrichtung zur mechanischen Zufuhr von Lösung zum Brenner bei der Flammenphotometrie und Absorptionsspektroskopie. Die Vorrichtung ermöglicht eine konstante Zufuhr und restloser Verbrauch der Lösung.

REFERENCE

1 D. COOKE, *14th L.S.U. Symposium on Analytical Chemistry*, Baton Rouge, January, 1961.

INFRARED STUDY OF THE COPPER–EDTA COMPLEX AND ITS REACTION WITH VARIOUS AMINO COMPOUNDS

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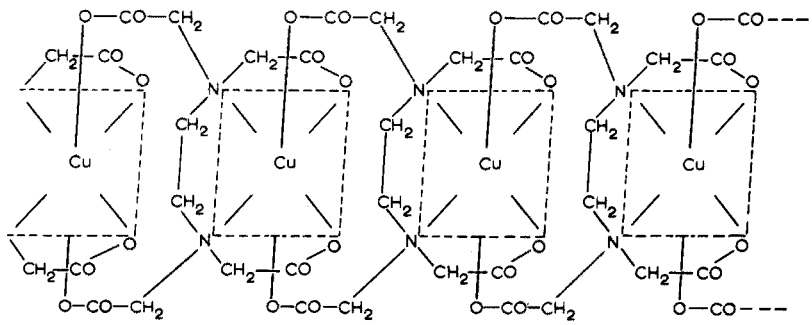
(Received August 21st, 1961)

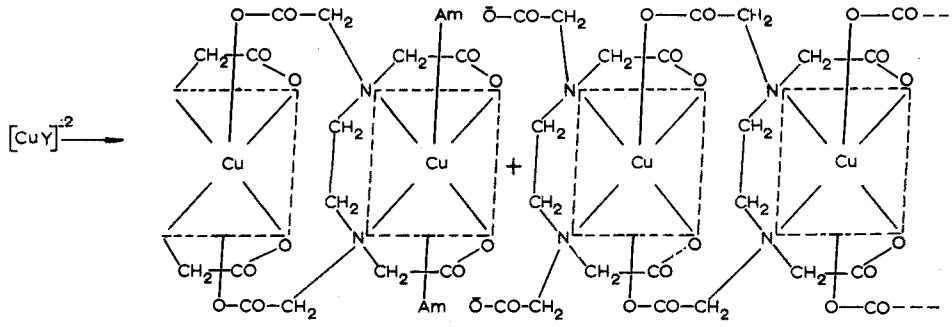
INTRODUCTION

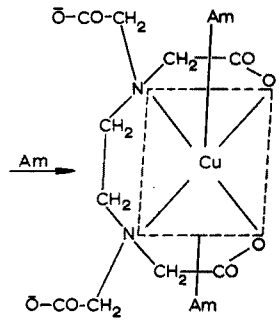
A spectrophotometric study of the copper–EDTA complex, $[CuY]^{-2}$*, and its behavior when amino compounds of various types are added to the complex in solution, was reported by KIRSON AND CITRON[1]. It was found that within a pH range of 4.0 to 11.0, $[CuY]^{-2}$ is stable. Addition of sodium hydroxide to a solution of this complex does not decrease the optical density at 720 mμ (wavelength of peak absorption in the visible) until pH 11.0 is reached and the complex $[Cu(OH)Y]^{-3}$ is thought to be formed. However, addition of ammonia and certain amino compounds to the complex reduced its optical density long before pH 11.0 was reached. The authors postulated that copper was hexadentate in the complex which existed as a polymer in solution, *viz.*



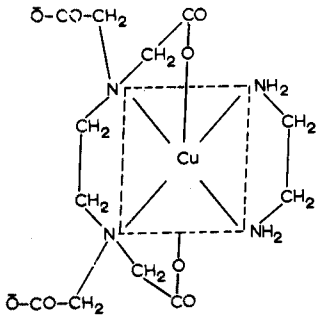
Ammonia, or certain amino compounds, then coordinated with the central copper in place of two carboxyl linkages, and thus disrupted the polymeric $[CuY]^{-2}$ into single molecular units of $[Cu(Am)_2Y]^{-2}$ with a resultant decrease in the optical density, *viz.*

* Y^{-4} = EDTA anion = $(^{-}O—CO—CH_2)_2—N—CH_2—CH_2—N—(CH_2—CO—O^{-})_2$





It was found that ammonia and primary amines (aliphatic) most readily combined with the $[CuY]^{-2}$, while secondary amines did this to a lesser extent, and tertiary amines and certain aromatic amines reduced the optical density only very slightly. Diamines, such as ethylenediamine, not only caused a decrease in the optical density, but also shifted the wavelength of absorption from 720 mμ to about 650 mμ (whereas the peak for $[Cu(en)_2]^{+2}$ absorption is at 540 mμ). This shift in wavelength suggested that upon addition of ethylenediamine, the following complex formed in solution:



In addition, the above authors found that amino compounds of the type $H_2N(CH_2)_nNH_2$ ($n \geqslant 3$) acted in the same manner as did primary amines, while polyamines, such as diethylenetriamine and triethylenetetramine, whose complexes with copper not only had very high stability constants, but presumably also formed polymers in solution,

at first seemed to coordinate with $[CuY]^{-2}$, but eventually pulled the copper away from the EDTA.

It seemed to the present author that an infrared study of the $[CuY]^{-2}$ complex alone and in conjunction with amino compounds of various types would reveal more evidence regarding the coordination of the amines with the copper in the complex. It was decided to form the complex stoichiometrically in aqueous solution in the pH region of about 6.0 to 8.0, then to freeze-dry aliquots of this solution to which exact stoichiometric amounts of amino compound had been added along with potassium bromide, and to press KBr-disks in which the $[CuY]^{-2}$ and presumed coordinated amine could be dispersed in solid form. It was assumed that the amino compounds themselves were so volatile that, unless they were coordinated with the copper–EDTA complex, they would be swept into the trap of the freeze-drying apparatus. An attempt to freeze-dry considerable quantities of the amines alone in potassium bromide solution indeed resulted in no detectable spectra, thus verifying the above assumption. Examination in solution, whether aqueous or organic, was discarded as a possible means of investigation, since it would be very difficult to determine conclusively whether the added amines were coordinated to the complex, or not.

EXPERIMENTAL

The exact experimental procedure was as follows: Into each of a series of freeze-drying tubes were pipetted 1.5 ml of bromide solution (300 mg of potassium bromide per ml of solution).

The $[CuY]^{-2}$ complex was formed by dissolving 3.7725 g of EDTA-disodium salt dihydrate in about 30 ml of solution, adding 2.2330 g of copper bromide and 20 ml of 1 *N* sodium hydroxide solution, mixing, and diluting to exactly 100 ml. The resulting solution was 0.1 *M* in $[CuY]^{-2}$.

In each case, 0.5 ml of the 0.1 *M* $[CuY]^{-2}$ solution was placed in a small beaker and mixed with 0.1 ml of 1 *M* solution of monoamine or 0.05 ml of 1 *M* solution of ethylenediamine. The pH was then carefully adjusted to range 6.0 to 8.0 by addition of several drops of 1 *N* hydrochloric acid. Aliquots of 0.06 ml of each solution containing $[CuY]^{-2}$ plus amine were added, each to a different freeze-drying tube containing potassium bromide solution.

In a second series, 0.02-ml aliquots of the $[CuY]^{-2}$ plus amine were added to freeze-drying tubes also containing 1.5 ml of the above bromide solution. The amino compounds tested were: NH_3, *n*-$C_3H_7NH_2$, *n*-$C_4H_9NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$, and $C_2H_4(NH_2)_2$.

All the freeze-drying tubes were attached to a freeze-drying apparatus along with a tube containing 0.02 ml of the $[CuY]^{-2}$ complex alone in potassium bromide, and with another containing only 1.5 ml of the bromide solution (to provide a reference disk of about 450 mg of potassium bromide). The solutions were all allowed to freeze-dry overnight.

From the resulting powders, disks were pressed in a die under vacuum, at a pressure of 115,000 pounds per sq. in., and the infrared spectra were charted by a Perkin-Elmer Model 21 instrument. The disk containing only 450 mg of potassium bromide was placed in the reference beam during each spectral run from 2.5 to 13 μ. The two series of spectral runs—one containing the observed compounds at three times the concentrations of those in the other series—served to bring out all absorption bands at concentrations at which they could best be examined.

DISCUSSION

The above experimental procedure resulted in a series of spectra which, when amino compounds had been added, revealed fundamental differences from the spectra of $[CuY]^{-2}$ alone at numerous absorption frequencies. These differences emphasized conditions which could only arise if the amino compounds had coordinated to the central copper in $[CuY]^{-2}$. The differences in the derived spectra will be evident by examination of Figs. 1–7, and by reference to the following discussion of the various bands in each of seven regions of the spectra (corresponding to the figures). The discussion also includes pertinent data for these bands listed by other authors. Each figure contains four separate pictures of the region in question, in order to avoid the confusion of crowding too many spectra on one chart. The seven compounds examined are lettered as follows in each of the seven spectral regions: (*a*) $[CuY]^{-2}$ alone, (*b*) $+NH_3$, (*c*) $+n\text{-}C_3H_7NH_2$, (*d*) $+n\text{-}C_4H_9NH_2$, (*e*) $+(C_2H_5)_2NH$, (*f*) $+(C_2H_5)_3N$, (*g*) $+C_2H_4(NH_2)_2$ — signifying in cases (*b*) through (*g*) addition of the amine to $[CuY]^{-2}$ before freeze-drying.

Region (1), 2.8 to 3.9 μ (Fig. 1)

A strong peak is observed at 3380 cm^{-1} (2.97 μ) which can be attributed to H_2O and to N—H stretching. This band is relatively small in (*a*) and (*b*), thus signifying no N—H stretch in (*a*), and relatively little in (*b*). The band broadens and deepens in spectra

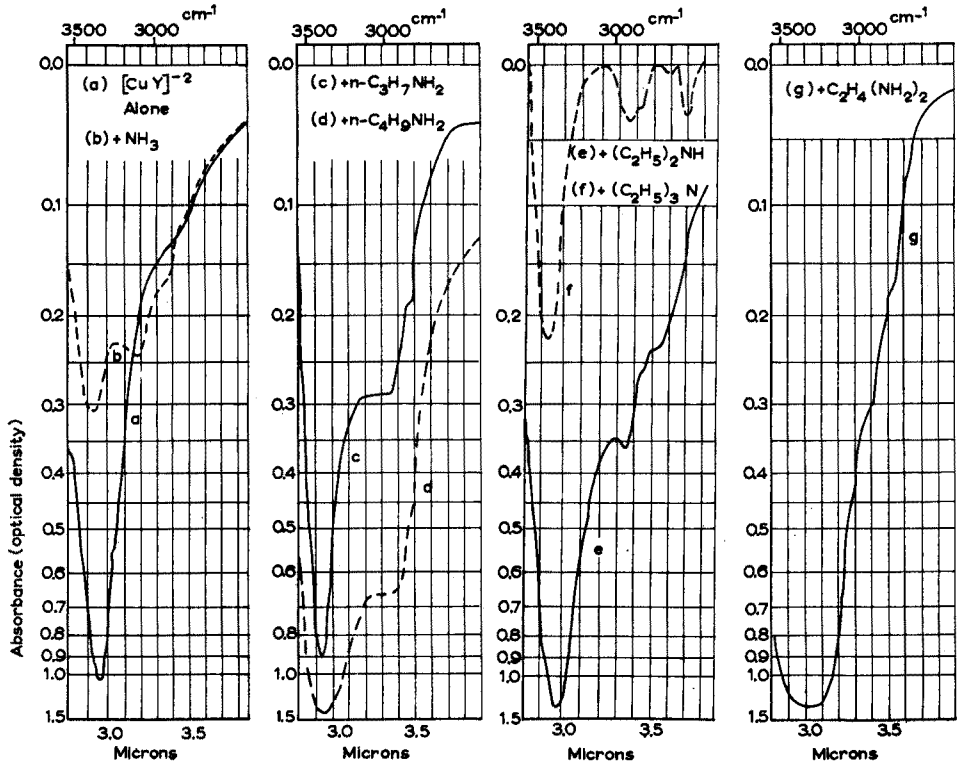


Fig. 1. Region (1), 2.8 to 3.9 μ.

(*c*) through (*g*), thus signifying considerable N—H absorption in addition to H_2O absorption. This band in the case of (*b*) would probably be very strong, but it is assumed that despite some coordination, most of the extremely volatile ammonia is swept away during the freeze-drying process.

A small shallow peak or shoulder is observed at about 3120 cm^{-1} (3.2 to 3.3 μ) in compounds (*b*) through (*e*), but not in (*a*) or (*f*). In (*g*), a broad band appears in this region. This small peak might be attributed[2] to NH_4^+ and AmH^+, or perhaps to ammonia or the amines coordinated to copper but with some hydrogen bonding to the resulting uncoordinated carboxyl. Such coordination would serve to weaken the N—H bands. The latter possibility is considered more likely since no peak at all is observed at 3120 cm^{-1} in (*f*), and since under the conditions of these experiments (pH, freeze-drying), formation of AmH^+ would be quite unlikely to occur.

In the 3.33 to 3.57 μ region (2800–3000 cm^{-1}), the following phenomena were observed: for (*a*) and (*b*), a slight depression at 2950 cm^{-1} which can be assigned to a $-CH_2-$ stretching frequency in the copper–EDTA; for (*c*), a shoulder at 2880 cm^{-1}, typical for n-$C_3H_7NH_2$[3]; for (*d*), a deeper and broader absorption at about 2900 cm^{-1}; for (*e*), definite shoulders at 2950 cm^{-1} and 2800 cm^{-1} — typical of secondary amines such as $(C_2H_5)_2NH$[4]; for (*f*), slight absorption bands at 2900, 2740, and 2670 cm^{-1} — typical of bands received with tertiary amines[5]; for (*g*), shoulders at 2950 cm^{-1} and 2830 cm^{-1}. The above spectra suggest that the amines are coordinated to the copper–EDTA complex, even in the case of tertiary amines to some degree. It would seem

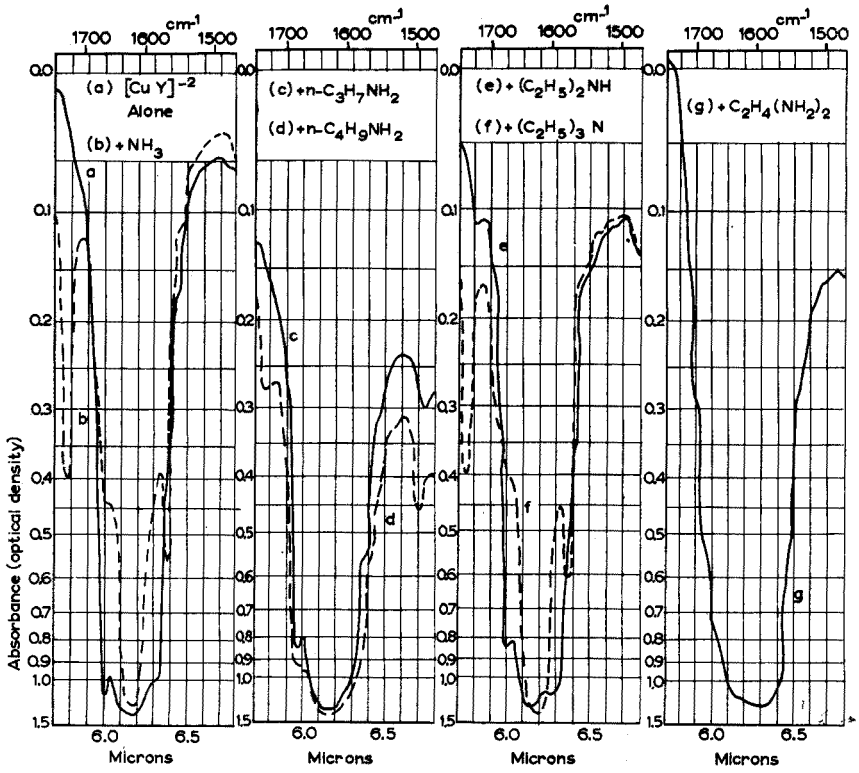


Fig. 2. Region (2), 5.7 to 6.8 μ.

likely that coordination of the amino group to the copper in the complex would not greatly change the typical frequencies of the —CH_2— stretching modes in the above amino compounds.

Region (2), 5.7 to 6.8 μ (Fig. 2)

Many vibrational modes contribute to the high density and consequential overlapping of absorption bands in this region. For instance $\rangle C{=}O$ stretching, —NH_2 deformation, and H—O—H bending frequencies occur in this region[6]. However, certain trends are noticeable in the spectra achieved here which may throw light on the structure of the complex dispersed in KBr.

For example, it is quite evident that if all the carboxyl groups of EDTA are coordinated to copper, a hexadentate complex will occur with a single $\rangle C{=}O$ stretching frequency in the 1600 cm^{-1} region[7]. This, in fact, seems to be the case in (*a*). Some band interference is of course present due to the —NH_2 deformation and H—O—H bending frequencies cited above. If uncoordinated carboxyl were present, which would be the case if the amines became coordinated to the copper, a second peak should be observable in the 1500–1650 cm^{-1} region [7,8]. This is evident in (*b*) through (*g*), at 6.4 to 6.45 μ, where there is absorption roughly proportional to the extent with which these amines are thought to enter the complex.

Another feature of this region is a sharp peak occurring at 1730–1740 cm^{-1} only in the cases where NH_3 or $(C_2H_5)_3N$ were added to the complex. This band is undoubtedly due to free carboxyl, —COOH, being present. A plausible explanation for this band appearing in the spectra of (*b*) and (*f*) is that the order of basicity of ammonia and amines are $NH_3 < R_3N \ll RNH_2 < R_2NH$[9]. Thus, the low basicity in the first two cases could give rise to the formation of some free carboxyl during the freeze-drying process. The extinction coefficient of this band is very high, and even a minute amount of free carboxyl present would give a sharp distinct peak.

Another occurrence in our spectra within this region lends credence to the arguments here presented. A band at 1485 cm^{-1} occurs in (*c*) and (*d*) only. This absorption can be attributed only to $H{-}\overset{H}{\underset{|}{N}}{-}C_nH_{(2n+1)}$, *i.e.*, to primary amines. That this band appears in (*c*) and (*d*) only, undoubtedly means that these compounds have coordinated with the copper in the complex, and have maintained this typical vibrational frequency.

Region (3), 6.8 to 7.7 μ (Fig. 3)

Reference can be found[10] to a small band due to chelated —CH_2COO^- at 1440 cm^{-1}. Such a band actually appears, to the greatest extent in (*a*), the spectrum of the $[CuY]^{-2}$ complex alone. The strength of this absorption diminishes in (*b*) through (*d*), but seems to increase somewhat in (*e*) and (*f*). It diminishes again in (*g*). This follows the presumption that in the $[CuY]^{-2}$ complex all the acetic acid groups are coordinated. When NH_3 or primary amines coordinate to the copper, much less coordinated —CH_2COO^- is present. With the secondary and tertiary amines, chelation of the —CH_2COO^- would increase again, while with ethylenediamine, chelation of this group would again decrease.

In $[CuY]^{-2}$, bands have been attributed[7] to $—COO^-$ at 1390 cm^{-1} and 1330 cm^{-1}. These bands appear in the spectra shown here. The band at 1390–1400 cm^{-1} is due to coordinated carboxyl. It is very deep in (*a*), diminishes from (*b*) through (*d*), and then deepens again in (*e*) and (*f*). In (*g*), the band diminishes in strength again. In most cases

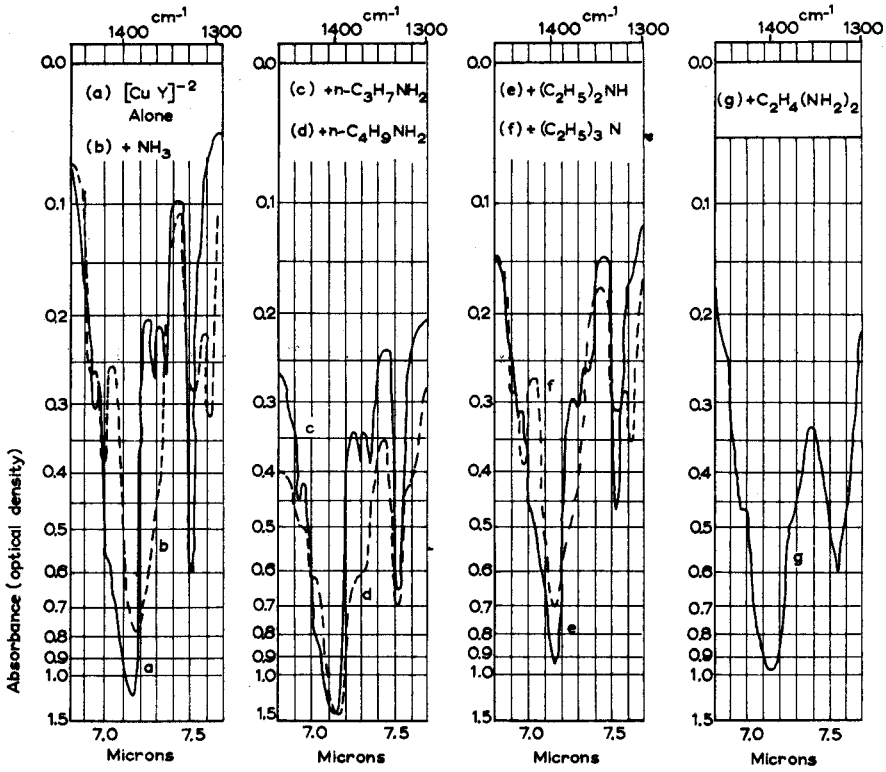


Fig. 3. Region (3), 6.8 to 7.7 μ.

where the band is weakest, there is a slight shoulder at 1380 cm^{-1}, indicating perhaps an absorption frequency due to uncoordinated carboxyl. In addition, in (*b*) and (*f*), where NH_3 or $(C_2H_5)_3N$ were added to $[CuY]^{-2}$, a sharp peak occurs at 1430 cm^{-1}. This is analogous to the sharp peak in the 1730–1740 cm^{-1} region, and is most likely due to the same cause — free carboxyl, —COOH, being present in these two cases. Twin peaks at 1360 cm^{-1} and 1370 cm^{-1} of lighter intensity, are probably due to $—CH_2$ deformations, and are sometimes masked because of the strong carboxyl peaks nearby. The $—COO^-$ peak at 1330 cm^{-1} is single in (*a*), but more or less split in the succeeding spectra, except in (*g*), where a broad band occurs. A second peak, when it occurs, appears at 1315 cm^{-1}, and is probably due to uncoordinated carboxyl.

Region (4), 7.7 to 8.7 μ (Fig. 4)

There are peaks at 1285, 1275, 1260, and 1245 cm^{-1} in all cases except (*f*) and (*g*). In (*f*) there is some absorption at 1275 and 1250 cm^{-1}, and a rather broad band at 1230 cm^{-1}. In (*g*), only two distinct peaks occur, at 1285 cm^{-1} and 1265 cm^{-1}. These

peaks are probably due to either C—N or —COO^- vibrational modes, or both[7], and are very difficult to interpret. The less complicated spectrum of (*g*) in this region might indicate a second ring formed by the coordination of ethylenediamine to $[CuY]^{-2}$ to form $[Cu(en)Y]^{-2}$ in which the C—N vibrational modes of the ethylenediamine ring would be much the same as those of the copper–EDTA complex proper.

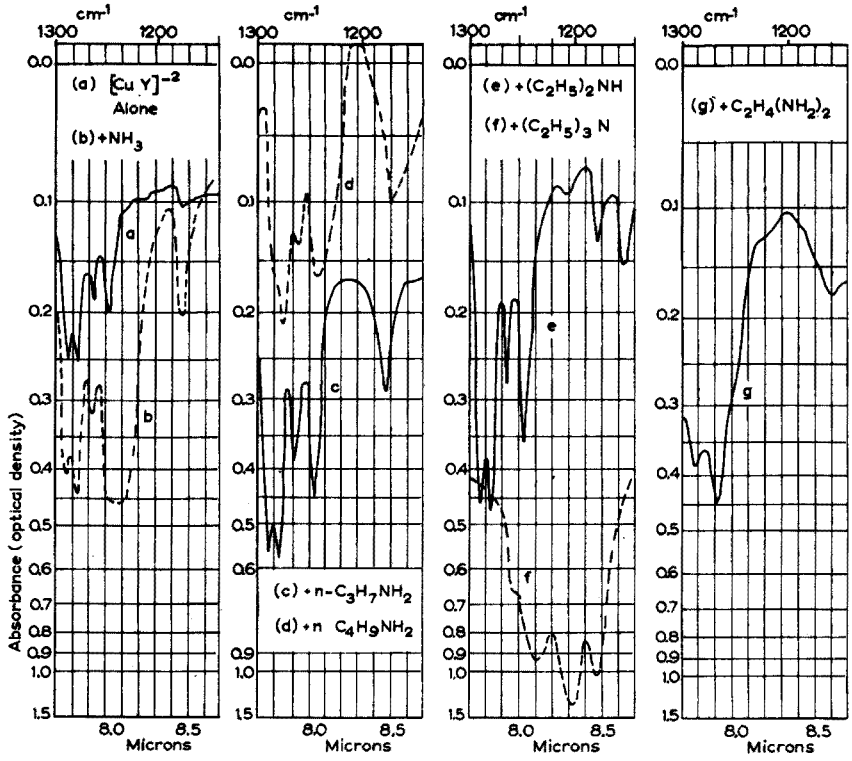


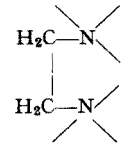
Fig. 4. Region (4), 7.7 to 8.7 μ.

There are several bands of varying intensity in the 1140–1210 cm^{-1} region, the most prominent of which is a sharp band at 1180 cm^{-1} in (*b*), (*c*), and (*d*). Hardly any absorption occurs in (*a*) in this region. In (*e*), (*f*), and (*g*), there are several bands in various places over the region. Exact assignment in this region is difficult, and will not be attempted here.

Region (5), 8.7 to 9.8 μ (Fig. 5)

There are small but sharp peaks at about 1113, 1100, and 1088 cm^{-1} which are attributable to C—N vibrational modes[7]. These occur in much the same manner in all the spectra from (*a*) through (*g*), except in (*f*) where a single band is detected at 1118 cm^{-1}. These bands vary in relative strength among themselves from compound to compound in (*a*) through (*g*), and sometimes are shifted slightly in frequency of absorption — but taken all together, the overall absorption in the region 1080–1120 cm^{-1} seems to remain about steady in (*a*) through (*g*). In $[CuY]^{-2}$, C—N bands exist

with varied environments, and this would be the case even more were amino compounds coordinated with the complex. For example the 1113 cm^{-1} band may be due to C—N in —N—CH_2—C(=O)—O^- (uncoordinated). This band is very small in $[CuY]^{-2}$, *i.e.*, in (*a*), but increases when amino compounds are presumed coordinated. The 1100 cm^{-1} band may be due to C—N in



It has about the same intensity in spectra (*a*) through (*f*), but increases relative to the other neighboring bands in (*g*) where an extra linkage of this type would be expected

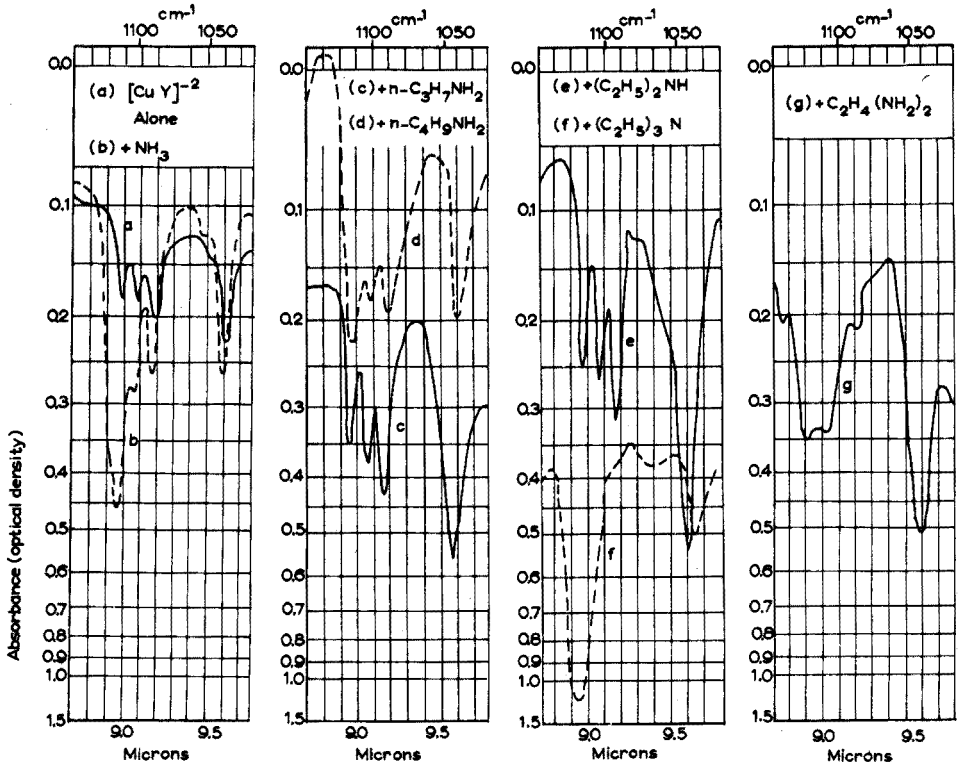


Fig. 5. Region (5), 8.7 to 9.8 μ.

due to ethylenediamine coordinated with the copper in the complex. It is difficult to correlate the size of the band at 1088 cm^{-1} with any particular type of C—N linkage.

A very sharp band due to a —COO^- vibrational mode occurs at 1040 cm^{-1}. This

band is probably due to uncoordinated carboxyl. It is very small in (*a*), increases in (*b*) through (*e*), decreases in (*f*), and increases in (*g*), as would be expected if the above assignment were correct.

Region (6), 9.8 to 10.9 μ (Fig. 6)

Small but sharply defined peaks appear at 1010, 998, 983, and 965 cm^{-1} for (*a*) through (*e*). These bands are not so sharply defined in (*f*). In (*g*), the bands occur at 1018, 988, 978, and 965 cm^{-1}. In this spectral region another deep band appears at

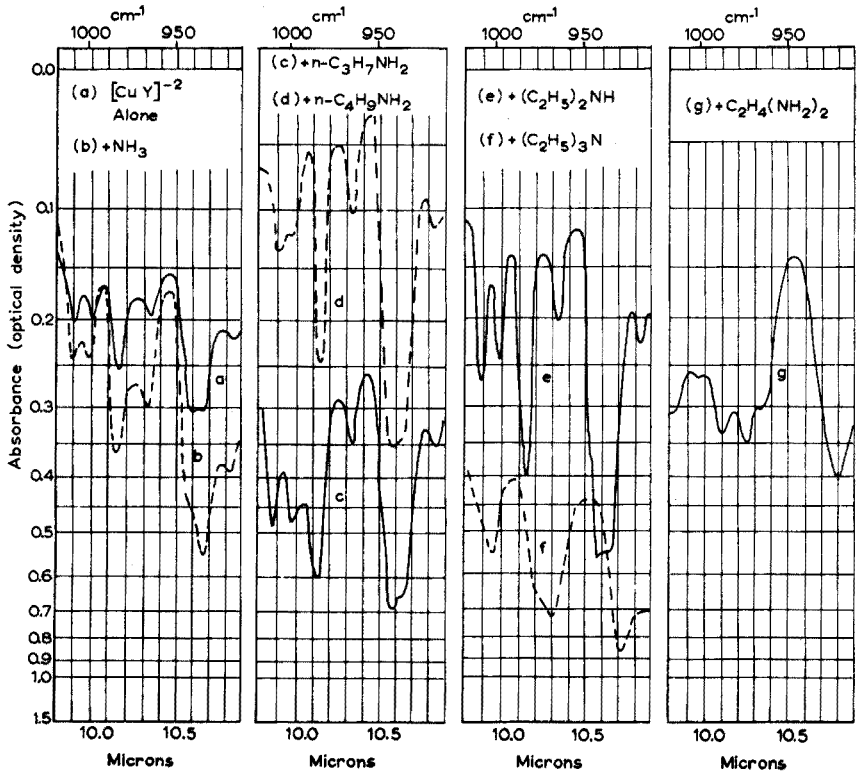


Fig. 6. Region (6), 9.8 to 10.9 μ.

940 cm^{-1} with a shoulder or second small peak at 918 cm^{-1}. In (*g*), this is a single band at 925 cm^{-1}. All the bands in this region are probably due[7] to —COO^-, but exact interpretation is difficult here, since coordinated H_2O may also show up in this region[11].

Region (7), 11.1 to 12.2 μ (Fig. 7)

In spectra (*a*) through (*f*), a strong band occurs at 853 cm^{-1}. This is due to a —COO^- vibration[7], probably coordinated carboxyl. A second, more shallow peak occurs in spectra (*b*) through (*e*), but not in (*a*) or (*f*), at 825 cm^{-1}. This is probably due to uncoordinated carboxyl, the extinction coefficient for this band presumably being smaller than for the band at 853 cm^{-1}. In spectrum (*g*), a broad deep absorption

occurs with a shallow peak at 845 cm^{-1}, and specific interpretation is difficult, except to say that ethylenediamine coordinated to copper would tend to give a broad band in this region.

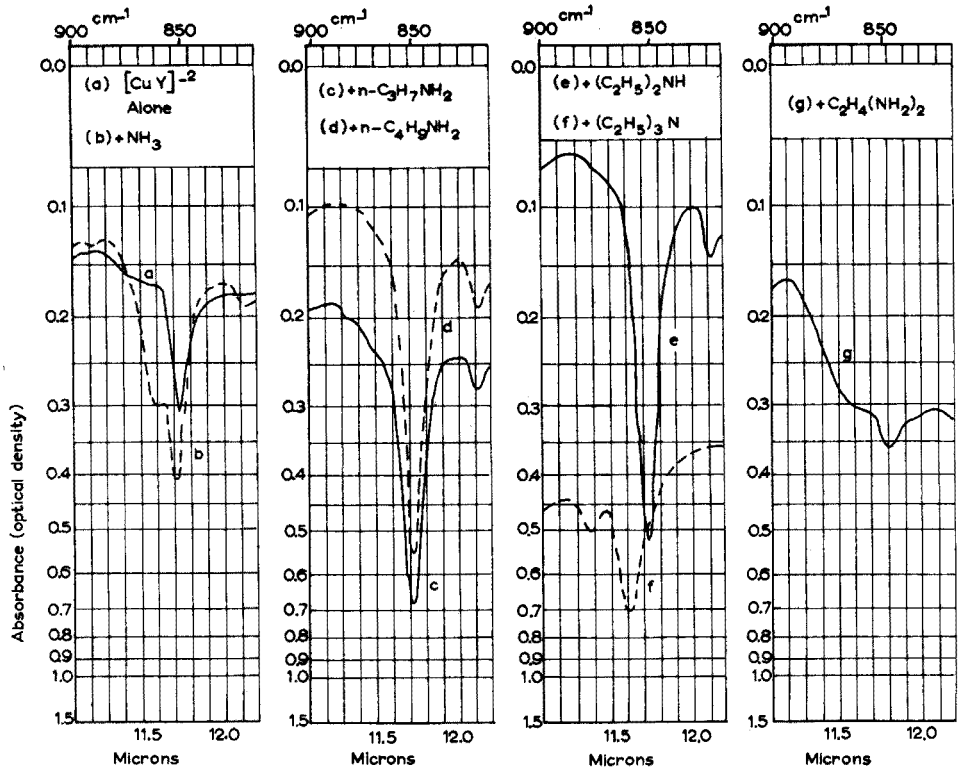


Fig. 7. Region (7), 11.1 to 12.2 μ.

CONCLUSIONS

An abundance of data derived from these spectra tends to verify that upon addition of ammonia and primary aliphatic amines to $[CuY]^{-2}$, these compounds disrupt two carboxyl groups from coordination with the central copper ion, and enter themselves into coordination with the copper, thus forming complexes of the general formula $[Cu(Am)_2Y]^{-2}$. With secondary amines, the same phenomenon occurs, but to a lesser degree. With tertiary amines, this occurs only at best to a very slight extent, because steric hindrance will not allow the amine successfully to approach the central copper. With ethylenediamine, $[Cu(en)Y]^{-2}$ is formed.

Amine salt formation with carboxyl groups is largely ruled out because the pH range (6.0–8.0) at which these experiments were carried out and the conditions of the freeze-drying process do not favor such an occurrence. Also, there would be no reason why tertiary amines such as $(C_2H_5)_3N$ would not just as readily form amine salts as primary amines. However, in the spectra shown here, there is considerable evidence that the bands peculiar to having had amines enter the complex are much less evident in the case of tertiary amine than in the case of primary or secondary amine, showing that tertiary amines do not enter the complex as readily only because they

cannot as easily reach the central copper ion. Also, in amine salts, the cations would easily be hydrolyzed and the volatile amines swept out of the system during the freeze-drying. The fact that the amino compounds are evident in the spectra at all, undoubtedly means that they have become coordinated to the central copper in a new type of complex.

Split bands in the carboxyl frequency regions show that both coordinated and uncoordinated carboxyl groups are present when amines have entered the complex, as contrasted to single sharp bands in the carboxyl regions for $[CuY]^{-2}$ alone showing that here all the carboxyl groups are coordinated to the central copper.

The phenomena observed here may have considerable value in the analysis for primary, secondary, or tertiary amines, and further investigation along this line seems warranted. It may also be useful to see what effects the copper–EDTA complex might have in coordinating with certain amino acids as opposed to not coordinating with others. Aromatic amines were not tested here at all, whereas various types of aromatic amines were tested by KIRSON AND CITRON[1]. No doubt, the effects of aromatic amines on $[CuY]^{-2}$ in the infrared should also be examined.

ACKNOWLEDGEMENT

The author would like to acknowledge the interest and support of Dr. A. L. UNDERWOOD, Dept. of Chemistry, Emory University.

SUMMARY

Verification in the infrared region is provided for a recent visible range spectrophotometric study which suggested that ammonia and certain amino compounds enter the $[CuY]^{-2}$ complex and coordinate with the central copper in place of two carboxyl linkages. Such coordination occurs to a lesser extent with secondary than with primary amines, but almost not at all with tertiary amines, presumably because of steric factors. The freeze-drying method was used to obtain the $[CuY]^{-2}$ complex alone, or with coordinated amines, dispersed in solid potassium bromide which was pressed into disk-form for infrared analysis.

RÉSUMÉ

Une étude du complexe cuivre–EDTA, par spectrophotométrie infra-rouge a montré que l'ammoniaque et certains composés aminés, se coordinnaient avec l'atome de cuivre central du complexe $[CuY]^{-2}$, à la place des 2 liaisons carboxyliques. Cette coordination se produit surtout avec les amines primaires et non avec les amines tertiaires.

ZUSAMMENFASSUNG

Es wird mit Hilfe der IR-Spektrophotometrie nachgewiesen, dass beim Kupfer–EDTA Komplex die Koordinierung nicht über Carboxylgruppen, sondern über Ammoniak bezw. Aminogruppen mit Kupfer als Zentralatom erfolgt.

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A SPECTROPHOTOMETRIC STUDY OF *o,o'*-DIHYDROXYAZOBENZENE AND ITS CHELATES WITH ALUMINUM, GALLIUM AND INDIUM

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INTRODUCTION

o,o'-Dihydroxyazo compounds have for some time found extensive use as chelating agents in certain analytical methods[1-4]. The compositions and stabilities of the chelates formed in solution by these compounds and divalent metal ions have been studied by others in some detail[5-9]. Previous investigations of the corresponding chelates formed in solution by trivalent metal ions have been largely limited to a few observations on metal-ligand ratios, and to some measurements of absorption and fluorescent spectra[10,11]. It was the purpose of the present investigation to determine the mode of chelation for *o,o'*-dihydroxyazobenzene with the trivalent ions of aluminum, gallium and indium, to establish the stabilities of these chelates, and to attempt to relate the stabilities to relevant properties of the metals.

EXPERIMENTAL

Apparatus and materials

Manual and automatic recording Beckman (DU) Quartz Spectrophotometers were used to measure absorbances. Matched 1-cm Corex cells were used as sample holders.

All pH measurements were made with a Beckman Model G pH meter which was calibrated with National Bureau of Standards aqueous buffer solutions. The recorded values of the pH refer to the "measured values", obtained in accordance with the calibration procedure used.

Water–ethanol mixtures, 35% in absolute ethanol by volume, were used as solvent. The water was deionized by passing distilled water through an Amberlite column. The conductance of this water was less than 1 μohm.

The *o,o'*-dihydroxyazobenzene was prepared in this laboratory by the method of WESELSKY AND BENEDIKT[12]. The purified product melted at 174° in a capillary and at 176° on a Koefler micro hot stage. The compound was further tested for purity by use of a chromatographic column packed with 100–200 mesh Florisil***. Development of the chromatogram with a 50% dioxane–methanol mixture produced only one band. Over the concentration range spanned in this investigation, *o,o'*-dihydroxyazobenzene was found to conform to Beer's law.

* Taken in part from the thesis submitted by J. R. KIRBY in partial fulfillment of the requirements for the Ph.D. degree in Chemistry at Duke University, June 1960. Present address: Chemstrand Research Center, Inc., Durham, North Carolina.

** Present address: Department of Chemistry, Boston University, Boston, Massachusetts.

*** Obtained from the Floridon Co., Warren, Penna. (U.S.A.)

Aluminum metal of 99.997% purity, obtained from the Aluminum Company of America, was dissolved in a minimum quantity of 6 *N* hydrochloric acid and the resulting solution used to prepare a stock solution which was $1.007 \cdot 10^{-2}$ *M* in aluminum. Gallium metal, obtained from Fisher Scientific Co., was found to be 99.9 (± 0.5)% pure by precipitation as the 5,7-dibromo-8-hydroxyquinolate[13]. A $4.99 \cdot 10^{-3}$ *M* stock solution was prepared by dissolving 0.3499 g of the metal in a minimum quantity of concentrated sulfuric acid and diluting to 1 l with water. Indium metal, also obtained from Fisher Scientific Co., was found to be 97.2(± 0.9)% pure by precipitation as the oxinate[14]. A $4.85 \cdot 10^{-3}$ *M* stock solution was prepared by dissolving 0.5739 g of the metal in a minimum quantity of concentrated nitric acid and diluting to 1 l with water.

The pH values of solutions used in the mole ratio and continuous variations studies were controlled with acetic acid–sodium acetate buffer or with excess hydrochloric acid. The acetate buffers were prepared from standardized reagent grade glacial acetic acid and carbonate free sodium hydroxide. A 0.249 *N* hydrochloric acid solution was prepared from reagent grade concentrated acid.

A large part of this investigation was conducted in the absence of any buffer. Desired variations in pH were obtained by adding dropwise quantities of sodium hydroxide or hydrochloric acid solutions.

A 1 *M* potassium chloride solution was used to maintain a constant ionic strength of 0.10 *M* for all the studies.

The equilibria were established in a room held in the vicinity of 25°, and the solutions were maintained at this temperature for the absorbance and pH measurements. The equilibria were sufficiently insensitive to any temperature variations (which in no cases exceeded $\pm 3°$) for the purpose of the study.

Determination of the first ionization constant of o,o'-dihydroxyazobenzene

For convenience, *o,o'*-dihydroxyazobenzene will be abbreviated as DHAB, and the specific undissociated and dissociated forms of the dye will be represented by H_2L, HL^- and L^{-2}.

A detailed spectral–pH study was made of DHAB in the absence of the trivalent cations. A 500-ml sample of $4 \cdot 10^{-5}$ *M* DHAB solution was placed in a beaker and continuously stirred while the pH, which was monitored with the pH meter, was varied from 3 to 12 by addition of dropwise quantities of sodium hydroxide or hydrochloric acid. At suitable pH values, aliquots of the solution were removed for observations on the absorption spectra. The absorbance was constant below pH 7, but in the range pH 7 to 10.6 the solution underwent a distinct color change from yellow to orange-red, while above pH 11.7 there was a slight transition to an orange-yellow color. For all solutions of pH less than 11.7 an isosbestic point was noted at 436 mμ, indicating the presence of just two DHAB species. Above pH 11.7 the absorption curves did not pass through this point, presumably because of the appearance of a third DHAB species. The bathochromic shift occurring as the pH is raised from 7 to 10.6 is attributed to the conversion of H_2L to HL^-. The constancy in the absorbance from pH 10.6 to 11.7 indicates that the DHAB is here essentially all in the HL^- form. The slight hypsochromic shift above pH 11.7 is interpreted to correspond to the transition of HL^- to L^{-2}. The absorbances of all solutions of pH < 12 were found to be constant for at least five and a half months. Because of the instability of DHAB at

pH > 12 and the uncertainty of measured pH values in this range, the absorption curve of the L^{-2} form of the dye was not obtained.

A wavelength of 500 mμ, which corresponds to the absorption region of the maximum difference in the extinction coefficients of H_2L and HL^-, was used to calculate the first ionization constant of DHAB. From the data plotted in Fig. 1. the measured pH at which $[H_2L]$ equals $[HL^-]$ is 9.3 and this value was taken as equal to pK_1*.

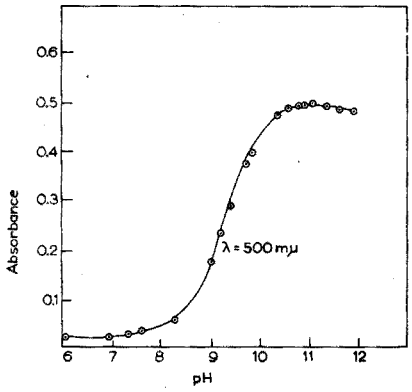

Fig. 1. The effect of pH on the absorbance of *o,o'*-dihydroxyazobenzene, $4.00 \cdot 10^{-5}$ *M* DHAB.

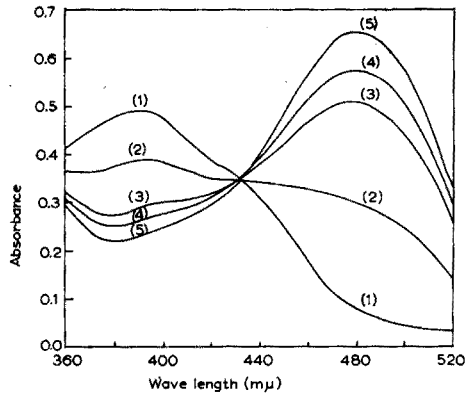

Fig. 2. Absorption spectra of $4.00 \cdot 10^{-5}$ *M* *o,o'*-dihydroxyazobenzene with varied amounts of total aluminum. pH 4.65. Al in $M \cdot 10^5$: Curve (1), 0.00; Curve (2), 1.60; Curve (3), 3.20; Curve (4), 4.00; Curve (5), 10.0.

Determination of the composition of the chelates

Spectral studies of solutions containing the chelates were restricted to pH values for which the free DHAB would exist only in the H_2L form (*i.e.*, pH < 7.5). The trivalent cations used are non-absorbing in the visible region of the spectrum, a fact which made it convenient to use them as the variable component in mole ratio studies. For the solutions which were investigated, the time required to allow the metal–DHAB equilibria to be established, as denoted by the constancy of the absorbance values, varied from approximately one week for aluminum, to less than a day for gallium, to less than 30 min for indium.

For each of the three metal–DHAB systems, chelation was accompanied by a pronounced bathochromic shift in the visible absorption spectrum. The magnitude of the shift was characteristic of the particular metal and the type of chelate formed. The largest shift in the maximum, and hence in the entire visible spectrum, was given by gallium, while indium caused the smallest shift.

Mole ratio studies. The absorption curves shown in Fig. 2 for the aluminum–DHAB system (pH 4.65) are typical of those obtained in a series of mole ratio studies. In this

* The equilibrium constants determined in the present study are practical constants, calculated from equilibrium concentrations of various DHAB species (obtained experimentally from spectra) and from apparent hydrogen ion concentrations (obtained experimentally from measured pH values, where the pH meter was standardized against aqueous buffers). For the particular solvent used, the apparent hydrogen ion concentrations will be proportional to and not greatly different from the true equilibrium concentrations.

particular study, there is an isosbestic point at 432 mμ. Two wavelengths were chosen for more detailed study; one where the chelate absorbed more than the DHAB alone (475 mμ) and one where the chelate absorbed less (390 mμ). A plot of the moles of aluminum against the absorbances is given in Fig. 3. In this plot the points are experimental values while the intersecting straight lines would be expected for an infinitely stable 1 : 1 chelate. Only the 1 : 1 chelate is indicated, it being somewhat dissociated under the conditions of experiment. The existence of the isosbestic point at 432 mμ is excellent evidence that only two DHAB species are present, H_2L and a single chelate. Similar mole ratio studies for the gallium and indium systems, conducted at the respective pH values of 2.50 and 5.45, revealed isosbestic points at 435 mμ for gallium and 428 mμ for indium. The gallium system gave, at the specified pH, a well defined break at the mole ratio corresponding to a 1 : 1 chelate.

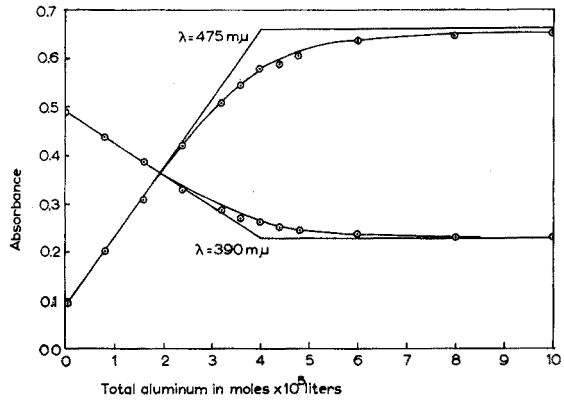

Fig. 3. Mole ratio plot of aluminum–*o,o'*-dihydroxyazobenzene. Aluminum variable component. $4.00 \cdot 10^{-5}$ *M* DHAB. pH 4.65.

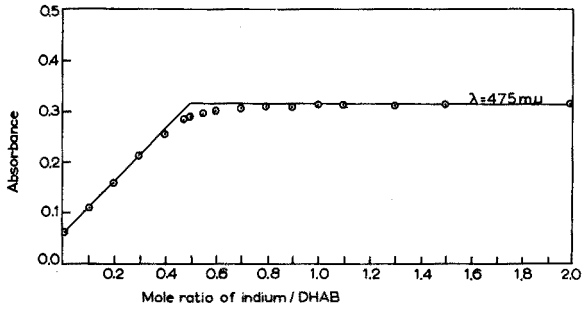

Fig. 4. Mole ratio plot of indium–*o,o'*-dihydroxyazobenzene. Indium variable component. $3.00 \cdot 10^{-5}$ *M* DHAB. pH 6.50.

In contrast to the fairly stable 1 : 1 chelates formed by gallium and aluminum, indium was observed to undergo no chelation below pH 4. Further, the mole ratio study for the indium system at pH 5.45 did not reveal a well defined break. However, an isosbestic point was found at 428 mμ indicating the presence of just two DHAB species. Proper interpretation as to the DHAB to metal ratio in the chelate formed

at this pH became possible only after a similar study of this system had been conducted at pH 6.50. At this latter pH an isosbestic point for all solutions was found at 434 mμ. From absorbance measurements made at suitable wavelengths, the usual mole ratio plot showed unequivocally the existence of a 2 : 1 chelate. There was no evidence for the 1 : 1 chelate at this pH. The isosbestic point found in this study was 6 mμ towards longer wavelengths from the isosbestic point found in the study at pH 5.45, which suggested that only H_2L and the 1 : 1 chelate were of significance at the lower pH. The mole ratio plot for the study at pH 6.50 is given in Fig. 4 as a typical example of the mole ratio studies which illustrate the existence of the 2 : 1 chelates.

Mole ratio studies with gallium at pH 6.20 indicated the presence of a 2 : 1 chelate for this system. An isosbestic point was found at 441 mμ. Mole ratio studies of the aluminum system at pH 6.50 indicated that an equilibrium existed between the 1 : 1 and 2 : 1 chelates under the conditions of experiment. With a stoichiometric dye concentration of $3.00 \cdot 10^{-5}$ *M*, the aluminum concentration was varied from 0 to $9.00 \cdot 10^{-5}$ *M*. The absorbances of all solutions with a mole ratio of metal to dye greater than 0.80 were identical at 508 mμ. The existence of this isosbestic point was interpreted as indicating that the extinction coefficients of the 1 : 1 and 2 : 1 chelates are identical at this wavelength and that no free dye existed at mole ratio values greater than 0.80. The absence of the isosbestic point at mole ratios <0.80 indicated the existence of free dye under these conditions.

Continuous variations studies. The method of continuous variations was used to study the aluminum–DHAB system at pH 4.65, 5.60 and 6.50, and the gallium–DHAB system at pH 6.28. At any particular pH, equimolar solutions of DHAB and

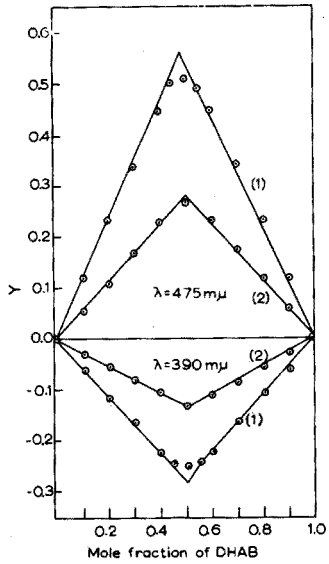

Fig. 5. Continuous variations plot of aluminum–*o,o'*-dihydroxyazobenzene. (1) pH 4.65; total *M* = *M* Al+*M* DHAB = $8.00 \cdot 10^{-5}$ *M*. (2) pH 5.60; total *M* = *M* Al+*M* DHAB = $4.00 \cdot 10^{-5}$ *M*

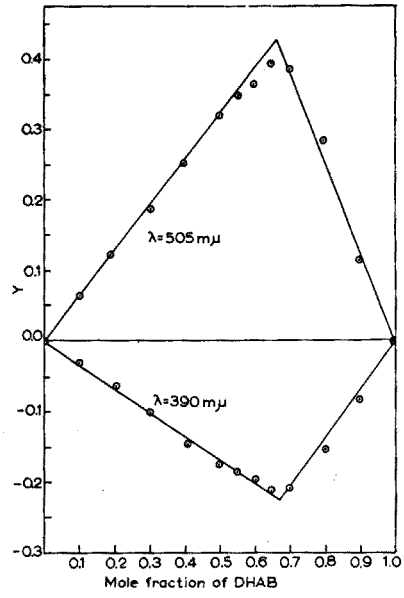

Fig. 6. Continuous variations plot of gallium–*o,o'*-dihydroxyazobenzene. pH 6.28; total *M* = *M* Ga + *M* DHAB = $5.00 \cdot 10^{-5}$ *M*.

metal were mixed in varying proportions, the total number of moles remaining constant. The absorbances of each solution were measured at selected wavelengths. The values of the absorbances calculated on the assumption of "no reaction" were then subtracted from the measured absorbances to give what are commonly referred to as *Y* values.

The application of the method to the aluminum system at pH 4.65 and 5.60 showed the DHAB to metal ratio to be 1 : 1. In the study of this system conducted at pH 6.50 the results were found to be dependent upon wavelength. Measurements made at wavelengths longer than 508 mμ gave a maximum in the continuous variations plot at 0.67 mole fraction DHAB, suggesting the existence of the 2 : 1 chelate. Application of the method at wavelengths less than 508 mμ gave maxima or minima at mole fractions between 0.50 and 0.67. These results suggest that the 1 : 1 and 2 : 1 chelates are in equilibrium under the conditions of experiment. The study of the gallium system at pH 6.28 gave results which were independent of wavelength. Maxima and minima in continuous variations plots were found at a composition corresponding to a DHAB to metal ratio of 2 : 1. Plots of *Y* values against mole fraction of DHAB, considered to be typical of the continuous variations studies, are shown in Figs. 5 and 6.

Determination of formulas and stabilities of the 1 : 1 chelates

For conditions under which the 1 : 1 chelates are the only DHAB complexes of importance, the species which may be present at significant concentrations will be the 1 : 1 chelate, H_2L, the solvated M^{+3} ion, and hydrolysis and chloride products of the M^{+3} ion.

Possible formulas for the 1 : 1 chelates are indicated by the following equilibria.

$$M^{+3} + H_2L \rightleftharpoons MH_2L^{+3} \quad (1)$$

$$M^{+3} + H_2L \rightleftharpoons MHL^{+2} + H^+ \quad (2)$$

$$M^{+3} + H_2L \rightleftharpoons ML^+ + 2\,H^+ \quad (3)$$

The number of hydrogens displaced upon chelation as well as the equilibrium constants may be determined by spectrophotometric–pH measurements[7]. The general equation for the formation of the 1 : 1 chelate may be written as:

$$M^{+3} + H_2L \rightleftharpoons MH_{(2-n)}L^{(3-n)+} + nH^+ \quad (4)$$

Letting $MH_{(2-n)}L^{(3-n)+}$ be represented by chelate-1:

$$K_1 = \frac{[\text{chelate-1}][H^+]^n}{[M^{+3}][H_2L]} \quad (5)$$

Taking logarithms and rearranging:

$$\log([\text{chelate-1}]/[H_2L]) = n\text{pH} - \text{p}K_1 + \log[M^{+3}] \quad (6)$$

Eqn. (6) predicts that a plot of $\log([\text{chelate-1}]/[H_2L])$ against pH should be a straight line of slope *n* provided the change in $\log [M^{+3}]$ is small over the pH range of the study.

Values of the ratio $[\text{chelate-1}]/[H_2L]$ were obtained from spectral measurements. For solutions containing only the 1 : 1 chelate the existence of isosbestic points in the vicinity of 430 mμ has been described. At shorter wavelengths than those of the isosbestic points the 1 : 1 chelates have smaller extinction coefficients than H_2L, the

maximum differences in the values occurring around 390 mμ. For this wavelength, and for other wavelengths where the unchelated metal does not absorb significantly and where the 1 : 1 chelate and H_2L have different extinction coefficients, it may be readily shown that

$$[\text{chelate-1}]/[H_2L] = (A_d - A_m)/(A_m - A_c) \quad (7)$$

where A_d is the absorbance of DHAB at a given stoichiometric concentration when in the form of H_2L, A_c is the absorbance of DHAB at the same stoichiometric concentration when in the form of the 1 : 1 chelate, and A_m is the absorbance of DHAB at the same stoichiometric concentration when distributed between the two forms. Eqn. (7) was used to obtain values of [chelate-1]/[H_2L] for each metal–DHAB system at a wavelength of 390 mμ.

For each DHAB–metal system, a 500-ml solution was prepared which was $3.00 \cdot 10^{-5}$ *M* with respect to DHAB and $5.00 \cdot 10^{-4}$ *M* with respect to metal. The amount of metal required to form a 1 : 1 chelate was thus only a small fraction of the stoichiometric concentration of metal. To prevent any precipitation, components of the solution were added in a definite order (*viz.* water, alcohol, potassium chloride, 3 drops of 6 *N* hydrochloric acid, DHAB, metal). The pH, which was monitored with the pH meter, was varied at will by addition of dropwise quantities of sodium hydroxide or hydrochloric acid. After the pH became constant at a desired value, a portion (approximately 10 to 15 ml) of solution was withdrawn for further study. The absorbances and pH values of solutions were checked periodically for a month and were found to be constant after attainment of equilibrium. The absorbances of these solutions at

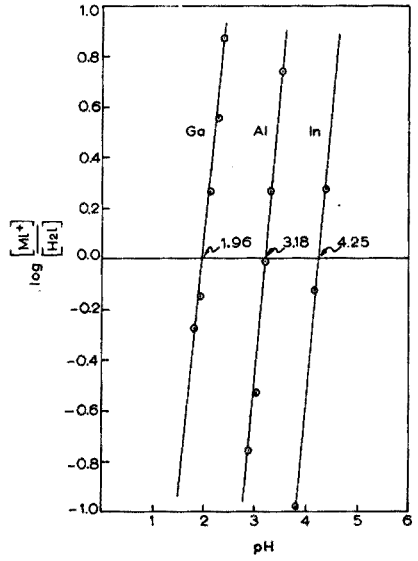

Fig. 7. pH–log [ML^+]/[H_2L] plot for determining pK_1 values of the metal–DHAB chelates. Slope of line for Ga–DHAB system = 1.9; for Al–DHAB system = 2.2 and for In–DHAB system = 2.2.

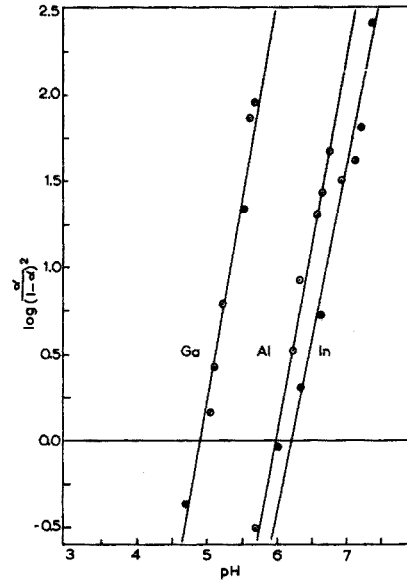

Fig. 8. pH–log $\alpha/(1-\alpha)^2$ plot for determining pK_2 values of the metal–DHAB chelates. Slope of line for Ga–DHAB system = 2.2; for Al–DHAB system = 2.1 and for In–DHAB system = 2.0.

390 mμ gave the A_a, A_c, and A_m values from which log ([chelate-1]/[H_2L]) values were calculated. Plots of log([chelate-1)/[H_2L]), given as log [ML^+]/[H_2L], against pH are shown in Fig. 7 for the aluminum–, gallium– and indium–DHAB systems. The slopes of the lines were found to be 2.2 for aluminum and indium, and 1.9 for gallium.

As has been indicated, the observed slopes will give the values of n under conditions where only small changes occur in the absolute values of log [M^{+3}]. The latter values will diminish somewhat with increasing pH, however, because of increased chelation of the metals and because of increased hydrolysis of the unchelated metals. The effect of increased hydrolysis, like that of increased chelation, could only result in the observed slopes being less than the theoretical slopes for constant values of log [M^{+3}]. The results, therefore, provide a clear indication that the chelation reaction should be represented by eqn. (3) rather than by eqns. (1) or (2). That the observed slopes are not significantly less than 2 also suggests that hydrolysis reactions are not responsible for the removal of major fractions of the metal ions over the pH ranges covered by the experiments. The pK_1 values for the formation of the 1:1 chelates were evaluated from eqn. (6) using a value of 2 for n. The values obtained for the aluminum, gallium and indium systems were, respectively, 3.1, 0.61 and 5.2. Any error in the pK values due to the neglect of competing hydrolysis reactions and complexing reactions of the chloride will not alter the conclusions with respect to the relative stabilities of the three 1:1 DHAB–metal complexes.

Determination of formulas and stabilities of the 2:1 chelates

For solutions of aluminum, gallium and indium in the presence of excess DHAB, the 2:1 chelates are formed at sufficiently high pH, as indicated by the mole ratio and continuous variation studies, and by the shift in the positions of the chelate absorption curves towards longer wavelengths on conversion of the 1:1 to the 2:1 chelates. Experiments in which the DHAB concentration was twice that of the metal showed that the conversion to the 2:1 chelate becomes essentially complete at pH values below those at which a significant proportion of free DHAB exists as the HL^- ion. This essentially complete conversion to the 2:1 chelate was demonstrated by a constancy in absorbance with increasing pH. Absorption curves obtained in this study demonstrated that only at wavelengths greater than 500 mμ was there a sufficient difference in the extinction coefficients of the 1:1 and 2:1 chelates to allow the determination of the degree of conversion of the 1:1 to the 2:1 chelate as a function of pH. The undissociated DHAB was known to exhibit practically no absorbance at wavelengths greater than 500 mμ, while none of the chelates absorbed significantly above 600 mμ. The wave-lengths chosen to study the degree of formation of the 2:1 chelates were 530 mμ for gallium and 525 mμ for aluminum and indium.

The following general equation may be used to represent the formation of the 2:1 chelates

$$ML^+ + H_2L \rightleftharpoons MH_{(2-n)}L_2^{(1-n)+} + nH^+ \qquad (8)$$

Denoting the equilibrium concentrations of the 1:1 and 2:1 chelates by [chelate-1] and [chelate-2], the equilibrium constant may be written:

$$K_2 = \frac{[\text{chelate-2}][H^+]^n}{[\text{chelate-1}][H_2L]} \qquad (9)$$

In the experiments conducted to establish the values of n and K_2, the stoichiometric concentration of DHAB was twice that of the metal ion. For these conditions, the measured stability constants for the 1 : 1 chelates indicate that there should be essentially no free metal present at pH > 4 for gallium, at pH > 5 for aluminum, and at pH > 6 for indium. These were the minimum pH values used, while the upper pH limit was in the vicinity of 8 to insure that essentially all unchelated DHAB would exist in the undissociated form.

For conditions where the only metal and DHAB species present at significant concentrations are chelate-1, chelate-2 and H_2L, it readily follows that

$$K_2 = \frac{[\alpha C_m][H^+]^n}{[C_m(1-\alpha)][C_d - C_m(1+\alpha)]}$$

where C_m is the stoichiometric concentration of metal, C_d is the stoichiometric concentration of DHAB, and α is the fraction of metal in the form of chelate-2. But experimentally $C_d = 2\,C_m$. Thus

$$K_2 = \frac{\alpha[H^+]^n}{C_m(1-\alpha)^2}$$

Taking logarithms and rearranging:

$$\log \frac{\alpha}{(1-\alpha)^2} = n\text{pH} + \log C_m - \text{p}K_2 \qquad (10)$$

Eqn. (10) predicts that a plot of $\log \alpha/(1-\alpha)^2$ against pH should yield a straight line of slope n. For each metal–DHAB system, values of α were obtained as a function of pH by spectral measurements using the expression

$$\alpha = (A_m - A_1)/(A_2 - A_1)$$

where A_1 is the absorbance of chelate-1 at a concentration C_m, A_2 is the absorbance of chelate-2 at a concentration C_m, and A_m is the absorbance of a mixture of chelate-1 and chelate-2 with a total stoichiometric concentration equal to C_m.

The stoichiometric concentration of DHAB was $6.00 \cdot 10^{-5}$ M, while the stoichiometric concentration of metal was in each case $3.00 \cdot 10^{-5}$ M. The experimental procedure was essentially the same as that used in establishment of the K_1 values. The absorbances and pH values of metal–DHAB solutions were found not to be a function of time once equilibrium had been attained (constancy in the values observed for periods up to a month).

Plots of $\log \alpha/(1-\alpha)^2$ against pH for the three systems are shown in Fig. 8. The slopes of the lines are 2.2, 2.1, and 2.0 for gallium, aluminum, and indium respectively, indicating that both of the phenolic hydrogens are displaced when the second DHAB molecule becomes bound to the metal. Substitution of the appropriate values into eqn. (10) permitted establishment of the pK_2 values for the three metal–DHAB systems. The pK_2 values obtained were 7.4 for aluminum, 5.2 for gallium, and 8.0 for indium.

DISCUSSION

The observed order of stability for both the 1 : 1 and 2 : 1 chelates of *o,o'*-dihydroxyazobenzene with the three trivalent metal ions is Ga > Al > In. It may be noted that

the same order of stability has been reported by IZATT *et al.*[15], for the 1:1 and 2:1 acetylacetonate chelates of these three metal ions in aqueous solution. But while studies by SCHWARZENBACH and co-workers[16] have established that in aqueous solution the ethylenediaminetetraacetic acid and 1,2-diaminocyclohexanetetraacetic acid chelates of gallium(III) are more stable than those of aluminum(III), SCHWARZENBACH has also recorded a result[17] (from unpublished work) which indicates that ethylenediaminetetraacetic acid chelate of indium(III) is more stable than the corresponding chelates with either of the other two metals. Among the halide complexes of the three metals ions[18], the formation constants for the 1:1 fluoride to metal complexes are observed to decrease in the order $Al^{+3} > Ga^{+3} > In^{+3}$. The fluoride complexes of these cations would be expected to be predominantly ionic.

Many attempts have been made to correlate the stabilities of metal ion complexes with such properties of the metals as electronic configurations, ionic charges and radii, ionization potentials, electronegativities, basicities, etc. A thorough discussion of such correlations is included in a recent review by ROSSOTTI[19]. It becomes clear, however, that no single set of properties for a group of metal ions of the type now being considered will be sufficient to explain the relative stabilities for a series of ligands which themselves possess markedly different characteristics. Thus, while consideration of the reciprocals of the radii (or the ionic potentials) of the trivalent aluminum, gallium and indium ions allows a rationalization of the formation constants for the 1:1 fluoride complexes, no such consideration can also be adequate to explain the formation constants for either the *o,o'*-dihydroxyazobenzene or the ethylenediaminetetraacetic acid chelates. When widely differing ligands are to be considered, the change in their nature must clearly also be taken into account. For any ligand, the relative stabilities of the complexes for a series of metals will depend upon the affinities of the ligand and each metal for the solvent and for each other (including both heat and entropy factors). In an attempt to rationalize the results discussed herein, one may be tempted to suggest that the gallium(III) ion is the optimum size for the coordination of such ligands as the doubly ionized *o,o'*-dihydroxyazobenzene and the acetylacetonate ion, or that the vacant orbitals of the gallium(III) ion are particularly suitable as acceptors for electrons from these two chelating anions.

As has been suggested to us, perhaps the most important difference between trivalent aluminum and gallium is the electronic configuration of the ions. The aluminum(III) is an s^2p^6 (inert gas) ion and gallium(III) is an $s^2p^6d^{10}$ (pseudo-inert gas) ion. Therefore, as gallium(III) is only slightly larger than aluminum(III), there will be less shielding of the nuclear charge in the gallium ion. This will enhance the σ-bonding for ligand to gallium(III) over that for aluminum(III). This effect tends to increase the covalency. The large size increase in indium(III) probably causes the trend to reverse. (Al^{+3}, 0.52 Å; Ga^{+3}, 0.60 Å; In^{+3}, 0.81 Å)[20].

While the quantitative establishment of the stabilities of complexes implies the determination of equilibrium constants, various other properties of metal-ligand systems may often be used as measures of the stabilities of the complexes contained therein. Thus, in using acetylacetone as an extracting agent for trivalent aluminum, gallium and indium, STEINBACH AND FREISER[21] found the order of extraction to be Ga > Al > In as the pH was increased. Since the pH at which each chelate is extracted is a function of the stability constant, this is also the order of stability. But in considering the *o,o'*-dihydroxyazobenzene chelates of these three trivalent metals in 34%

N,N-dimethylformamide in water as solvent, FREEMAN AND WHITE[11] assumed that the magnitude of fluorescence intensity at the pH of maximum fluorescence could be taken as a measure of the relative stabilities of the chelates, and hence concluded that the stability decreased in order Al > Ga > In. It can be argued, however, that the pH of maximum intensity of fluorescence should be a better index to the relative stability of the chelates than the fluorescence intensity at this pH, since the position of equilibrium is dependent on the pH. SCHATZBERG[10], using this premise, had predicted that the gallium chelate would be the most stable.

It is of interest to consider a possible correlation between the stabilities and the absorption spectra of the chelates. Removal of the first proton from *o,o'*-dihydroxyazobenzene (H_2L) is accompanied by a bathochromic shift of about 100 mμ in the maximum of the visible absorption band, while partial conversion of the HL^- to L^{-2} is accompanied by a slight hypsochromic effect. It is not unexpected that a bathochromic shift in the absorption band maximum of H_2L would occur upon its chelation with a metal, since displacement of the two phenolic hydrogens accompanies the chelation process. But the observed bathochromic shift accompanying the chelation of any of the three metals is too large to be accounted for by the simple removal of the phenolic hydrogens. The shift in the absorption band maxima for both the 1:1 and 2:1 chelates was found to be in the order Ga > Al > In, which is the same order as the stabilities of the chelates. Since none of the three solvated metal ions absorbs in the visible region, the characteristic visible absorption spectra of the metal chelates may be interpreted as arising through the influence of the metals on the spectra of the L^{-2} ion. The observed positions of the absorption bands for the chelates suggest that the vacant orbitals of the gallium(III) ion may be better than those of either the aluminum or the indium ions as acceptors for electrons from the L^{-2} ion, since a larger donation of electrons to a metal acceptor would be expected to produce lower excited states for the chelate, and hence greater shifts towards the red end of the spectrum. Alternatively stated, the spectral observations suggest that the gallium chelates of *o,o'*-dihydroxyazobenzene possess a greater degree of covalent character than the corresponding chelates of either aluminum or indium. Such views are in line with recorded interpretations for the spectra of certain other metal chelates[22]. The suggestion that in the complexes of *o,o'*-dihydroxyazobenzene the ability of the trivalent metal ions to act as electron acceptors decreases in the order Ga > Al > In, is in line with the observed order of stabilities for the chelates.

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SUMMARY

The composition of the chelates of aluminum, gallium and indium with *o,o'*-dihydroxyazobenzene has been established in acidic alcoholic–water mixtures to be pH dependent by means of spectrophotometric measurements. Only chelates with a 1:1 and 2:1 ratio of *o,o'*-dihydroxyazobenzene to metal are formed. The first acid dissociation constant of *o,o'*-dihydroxyazobenzene and the formulas and stability constants for the chelates were determined. The stability of the chelates increased in the order indium, aluminum, gallium.

RÉSUMÉ

Les auteurs ont effectué une étude spectrophotométrique de l'*o,o'*-dihydroxyazobenzène et de ses chélates avec l'aluminium, le gallium et l'indium. On a pu déterminer la première constante de dissociation acide de l'*o,o'*-dihydroxyazobenzène et les constantes de stabilité de ces chélates. Leur stabilité augmente dans l'ordre In, Al, Ga et leur composition dépend du pH.

ZUSAMMENFASSUNG

Es wurde die Zusammensetzung der Chelate von Aluminium, Gallium und Indium mit *o,o'*-Dihydroxyazobenzol mit Hilfe der Spektrophotometrie untersucht. Ferner wurde die erste Säure-Dissoziationskonstante des *o,o'*-Dihydroxyazobenzols, sowie die Formeln und Stabilitätskonstante der Chelate bestimmt. Die Stabilität der Chelate nimmt zu in der Reihenfolge: Indium, Aluminium, Gallium.

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SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM AS VANADIUM(IV) PYRIDINE THIOCYANATE*

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INTRODUCTION

Vanadium thiocyanate complexes have been studied in aqueous solution[1-3]; FURMAN AND GARNER[4] established the presence of $VOSCN^+$ and indicated that higher complexes may be formed. Spectrophotometric methods for vanadium dependent on the absorption properties of the blue vanadyl ion[5] and of vanadyl thiocyanate in aqueous solutions[6] and in acetone–water solutions[7] have been developed. BAIRD[8] studied the pyridine thiocyanate complexes of several divalent cations and developed analytical procedures for the determination of copper, cobalt, nickel, iron(II) and manganese. He noted that vanadium formed a pyridine thiocyanate complex under different conditions. The distinctive properties of the vanadium complex suggested that further study of the system might lead to the development of a spectrophotometric method for vanadium determination.

APPARATUS

Spectral curves were made on a Beckman Model DK-1 recording spectrophotometer. Analytical measurements were made with a Beckman Model DU spectrophotometer. Stoppered silica cells of 1.00-cm optical path were used for all measurements. The apparatus and procedure for the separation of vanadium by electrolysis at a mercury cathode were similar to those used by LINGANE AND MEITES[9].

REAGENTS

Standard vanadium(IV) solution. For preliminary investigations, a solution of vanadium(IV) was prepared by dissolving purified vanadyl sulfate dihydrate in distilled water. The solution was standardized by titration with standard potassium permanganate[10]. Appropriate dilutions of the stock solution were made as needed.

Standard vanadium(V) solution. A standard vanadium(V) solution containing 1000 μg of vanadium per ml was prepared by dissolving 0.2296 g of reagent grade ammonium vanadate in a small volume of 2 *M* sulfuric acid and diluting to 100 ml with distilled water. Solutions of appropriate concentrations were prepared by volumetric dilution.

Sodium thiocyanate solution. A 9.0 *M* solution was prepared from the reagent grade salt.

* Condensed from a dissertation submitted by LUCY E. SCROGGIE to the graduate school of The University of Texas in partial fulfillment of the requirements for the doctor of philosophy degree, August 1961.

Pyridine and chloroform. Reagent grade pyridine and U.S.P. chloroform were used as received. A 50% solution of pyridine in chloroform was prepared by mixing equal volumes of the two liquids.

RECOMMENDED PROCEDURE

Transfer a volume of standard solution or sample for analysis containing 400 to 1200 μg of vanadium to a 30-ml separatory funnel and add water as necessary to give a total volume of 5 ml of aqueous solution. Add 1.0 ml of 1.0 *M* hydrochloric acid and 5.0 ml of 9.0 *M* sodium thiocyanate solution. Mix by swirling. Add 5.0 ml of 50% pyridine–chloroform and stopper the funnel. Shake for 15 sec. After phase separation, drain the chloroform solution through a small piece of absorbent cotton in the tip of the funnel stem directly into the absorption cell. Measure the absorbance of the sample solution against a blank at 740 mμ. The system conforms to Beer's law.

LINGANE AND MEITES[9] have developed a separation of vanadium from many interfering elements by electrolysis at a mercury cathode. This method proved satisfactory as a separation prior to analysis by the recommended procedure.

EXPERIMENTAL

Absorption curves

The spectral curves of the vanadium(IV) pyridine thiocyanate complex in chloroform and of the blank over the spectral range of 400 to 800 mμ are shown in Fig. 1. The distinctive peak near 740 mμ was chosen for analytical measurements. The tail of this peak becomes a shoulder with maximum absorbance near 585 mμ as the

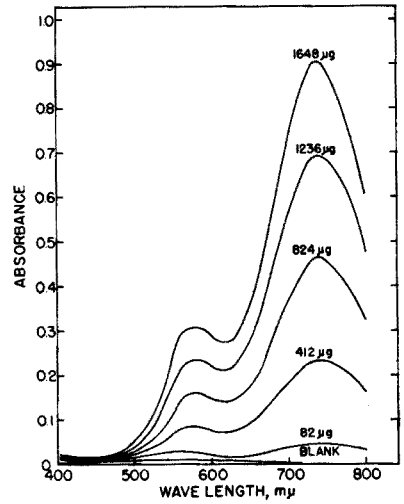

Fig. 1. Spectral curves of vanadium(IV) pyridine thiocyanate in chloroform.

vanadium present is increased above a total of 300 μg. BAIRD[8] reported also an absorption peak near 334 mμ.

During the investigation it was found that vanadium(V) was reduced by the sodium thiocyanate, which was added in large amounts in order to obtain full color

development. The absorption spectrum of the complex extracted from solutions initially containing vanadium(V) was identical with that obtained from vanadium(IV). In studying the influence of variables, samples were prepared from both vanadium (IV) and vanadium(V). The same conditions for optimum color development were found to be applicable to both initial oxidation states.

Efficiency of extraction

The extent of extraction was investigated quantitatively by developing the color of vanadium(IV) thiocyanate in the aqueous phase after extraction by the recommended procedure, according to the method given by SANTINI, HAZEL AND MCNABB[5]. An average of 6 μg of vanadium was detected in the aqueous phases after extraction of three separate solutions containing 1000 μg of vanadium. Considering the reliability of this method, more than 99.4% of the vanadium is extracted.

TABLE I

EFFECT OF EXTRACTION TIME

Extraction time (min)	*Absorbance at 740 mμ*	
	Vanadium(IV) 824 μg	*Vanadium(V) 1000 μg*
0.25	0.446	0.552
0.50	0.440	0.552
1.0	0.444	0.550
2.0	0.442	0.552
3.0	0.447	0.552
4.0	—	0.552

TABLE II

EFFECT OF HYDROCHLORIC ACID CONCENTRATION

HCl conc. M	*Absorbance at 740 mμ*
0.032	0.394
0.062	0.447
0.091	0.450
0.118	0.452
0.167	0.457
0.200	0.458

Extraction time

The absorbance of vanadium(IV) pyridine thiocyanate in chloroform as a function of extraction time is shown in Table I. The absorbance was essentially constant for extraction times ranging from 15 sec to 4 min. The shortest period for reproducible quantitative extraction, 15 sec, was chosen for the recommended procedure and was found to be sufficient for all situations encountered in the course of this research. Mechanical shaking is not necessary.

Hydrochloric acid concentration

The effect of hydrochloric acid concentration of the aqueous solution before extraction is shown in Table II. The absorbance of the chloroform solutions increased as the

acidity increased and became essentially constant for concentrations above 0.1 *M*. Addition of 1.0 ml of 1.0 *M* hydrochloric acid to the initial 5-ml sample volume gave reproducible absorbance values, and this concentration was adopted for the recommended procedure.

Sodium thiocyanate concentration

The absorbance of vanadium(IV) pyridine thiocyanate in chloroform as a function of sodium thiocyanate concentration in the aqueous phase before extraction is given in Table III. After a rapid initial increase, the absorbance became essentially constant after a concentration of 3 *M* was reached. A concentration of 3.75 *M*, obtained by adding 5.0 ml of 9.0 *M* sodium thiocyanate to the acidified sample solution, is recommended.

TABLE III

EFFECT OF SODIUM THIOCYANATE CONCENTRATION

Vanadium(IV) present, 824 μg

NaSCN conc. M	*Absorbance at 740 mμ*
0.38	0.367
0.68	0.383
1.12	0.410
1.42	0.419
1.64	0.430
1.81	0.442
2.85	0.446
3.08	0.451
3.29	0.452
3.48	0.452
3.63	0.454
3.75	0.454

TABLE IV

EFFECT OF AMOUNT OF PYRIDINE IN CHLOROFORM

Vanadium(IV) present, 824 μg

Pyridine (%)	*Absorbance at 740 mμ*
5	0.227
10	0.333
15	0.343
20	0.347
25	0.352
30	0.358
40	0.391
50	0.454

Amount of pyridine in chloroform

The effect of the percentage of pyridine in chloroform is shown in Table IV. Maximum absorbance was attained by extraction with a 50% pyridine–chloroform solution.

Color development and stability

The absorbance of a solution containing 824 μg of vanadium(IV) became essentially constant at 0.443 $\pm$ 0.002 after 7 min (measured from the start of the shaking period), and remained at this value for at least 3 h. At the end of 24 h the absorbance had increased to 0.455, a change of only 4.5%.

Range, accuracy and sensitivity

The absorbance of vanadium(IV) pyridine thiocyanate in chloroform as a function of the amount of vanadium(IV) or vanadium(V) taken for analysis follows a straight line relationship, obeying Beer's law for amounts of vanadium up to about 1800 μg in the initial 5.0 ml of solution taken for analysis. Following AYRES' treatment[11], the concentration range of best accuracy (for 1.00-cm cells) is from about 400 to 1200 μg of vanadium, or from 80 to 240 μg of vanadium per ml in an initial sample volume of 5.0 ml. Considering the reliability of the absorbance measurements, the relative analysis error is about 0.6%.

Three solutions containing 2 μg of vanadium in an initial volume of 5.0 ml gave an average absorbance of 0.001 in 1.00-cm cells. The sensitivity of the method, as defined by SANDELL[12], is 0.4 μg of vanadium per cm^2 at 740 mμ. The specific absorptivity, calculated from all data for construction of the calibration curve, is (2.80 $\pm$ 0.03)$\cdot 10^{-3}$ ml μg^{-1} cm^{-1}.

Reproducibility

The absorbances obtained for 6 aliquots of 5 different vanadium concentrations, with the associated mean absorbances and standard deviations, are shown in Table V. Standard deviations of 0.001 or 0.002 in measured absorbances were realized.

TABLE V

REPRODUCIBILITY OF ABSORBANCE

Vanadium present (μg)	*Absorbance at 740 mμ*			*Mean*	*Std. Dev.*
165	0.089	0.087	0.086		
	0.086	0.088	0.052[a]	0.087	0.001
330	0.175	0.175	0.176		
	0.177	0.177	0.179	0.177	0.002
494	0.261	0.261	0.263		
	0.263	0.262	0.263	0.262	0.001
659	0.357	0.356	0.357		
	0.357	0.356	0.357	0.357	0.001
824	0.445	0.444	0.444		
	0.445	0.444	0.443	0.444	0.001

[a] Rejected

Effect of foreign ions

Metal ions for these tests were used in the form of readily available soluble salts. Interference tests were made on solutions containing 824 μg of vanadium(IV) and 1000 μg of metal ion. From the absorbance obtained by the recommended procedure, the percentage of the vanadium recovered was calculated, and the tolerance limits

were calculated as the amounts of foreign ion producing 1% error in the vanadium recovery. Ethylenediaminetetraacetic acid (EDTA) reduces the interference of most of the metal ions; the interference tests were repeated on solutions containing 1.0 ml of 0.001 *M* EDTA in addition to the stated amounts of vanadium(IV) and metal ions, and the tolerance limits were calculated as before. The tolerance limits are given in Table VI.

TABLE VI

TOLERANCE LIMITS OF FOREIGN IONS

Vanadium(IV) present, 824 μg

Metal ion	*Tolerance limit, μg*	
	No EDTA	*EDTA present*
Silver(I)	1110	5000
Calcium(II)	>1000	910
Cadmium(II)	910	1430
Cobalt(II)	1430	830
Chromium(III)	430	5000
Copper(II)	50	570
Iron(II)	190	770
Iron(III)	40	50
Mercury(II)	1110	5000
Magnesium(II)	5000	5000
Manganese(II)	430	5000
Molybdenum(VI)	830	830
Nickel(II)	280	5000
Lead(II)	430	>1000
Tin(II)	500	310
Titanium(IV)	500	830
Zinc(II)	1100	>1000

TABLE VII

EFFECT OF IRON(III)

Vanadium(IV) present, 824 μg

Iron(III) added (μg)	*Absorbance at 740 mμ*
0	0.453
10	0.450
50	0.438
100	0.421
200	0.390
300	0.308
400	0.257
500	0.224
600	0.210
800	0.249
1000	0.348

Iron(III) is the notable interference, and various reducing agents and masking agents were studied to determine their results in minimizing its effect. None of the

reducing agents, including hydrazine sulfate, hydroxylamine hydrochloride and tin(II) chloride, or of the masking agents commonly recommended for this purpose, including citrate and phosphate, reduced the interference of iron(III) without having some adverse effect on the absorbance of the vanadium(IV) pyridine thiocyanate.

Mixtures of vanadium(IV) and various amounts of iron(III), and also pure iron(III) solutions, were treated by the recommended procedure and the spectra of the chloroform extracts were obtained. The effect of various amounts of iron(III) on the absorbance of vanadium(IV) pyridine thiocyanate is given in Table VII. Iron(III) present below the 200-μg level causes a relatively slight decrease in absorbance, but the large decrease caused by between 200 and 600 μg and the sharp increase beyond the 600-μg level were quite unexpected and, as yet, are unexplained.

The simple, relatively rapid and effective separation of vanadium from iron (and most other metal ions) by electrolysis at a mercury cathode[9] is recommended.

Anions that gave no interference were chloride, nitrate, sulfate, phosphate, and sulfite.

Application

National Bureau of Standards chromium–vanadium steel sample 30d was analyzed for vanadium by the recommended procedure preceded by electrolytic separation. The means of triplicate analysis of four weighed samples were 0.197, 0.180, 0.176, and 0.178% vanadium; the average was 0.183%, and the standard deviation was 0.009%, as compared with the certificate values of 0.190% and 0.004%, respectively.

DISCUSSION

The blue vanadium(IV) pyridine thiocyanate complex that has been used as the basis for a spectrophotometric determination of vanadium[5] cannot be extracted from acidic aqueous solutions into chloroform in the absence of pyridine, and thiocyanate ion must be added in excess before pyridine (in the form of a 50% solution in chloroform) to prevent the precipitation of the hydrous oxides of vanadium.

Chloroform is the best and most convenient of several water-immiscible organic liquids studied. The blue color forms immediately and extracts readily. It is very stable in the chloroform solution, which is in actuality a mixture of pyridine and chloroform; much of the pyridine is distributed into the aqueous phase and this phase must be very acidic initially to prevent the precipitation of vanadium. While the absorbance of the extracted complex increases as the percentage of pyridine in the extracting phase increases, this may be due to the fact that more pyridine is distributed into the aqueous phase, giving an effective concentration of the complex in the chloroform phase. In fact, after extraction with 60% and 70% pyridine–chloroform solutions, the volumes of the chloroform phase were insufficient to fill the absorption cells to the necessary level for absorbance measurement.

The large excess of thiocyanate is required for maximum and reproducible color development and for reduction of vanadium(V) to vanadium(IV) at room temperature. The recommended molar ratio of thiocyanate to vanadium of about 200 to 1 contrasts markedly with the stoichiometric amount reported by DESMUKH AND TATWAWADI[6] to be required for reduction at 80°. Spectral curves of the chloroform extracts obtained by applying the procedure to solutions initially containing vanadium as vanadium(V) were identical to those from vanadium(IV) solutions.

The rapid development of maximum absorbance and the constancy of absorbance with time indicate that time is not a critical factor in the determination.

A large quantity of vanadium(IV) was treated by the recommended procedure and the resulting complex was isolated by evaporation of the solvents, was purified by double recrystallization, and dried. Elemental analysis of the solid was as follows: C, 48.52%; H, 3.50%; N, 16.74%; S, 16.02%; vanadyl (by difference), 15.22%. This composition corresponds to a complex having the formula $VO(C_5H_5N)_2(SCN)_2 \cdot C_5H_5N$.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support of the University Research Institute, project number R-223.

SUMMARY

A spectrophotometric determination of vanadium as vanadium(IV) pyridine thiocyanate is described. The blue complex is formed in acidic aqueous solution and extracted into pyridine–chloroform. Absorbance is measured at 740 mμ. The range of best accuracy for 1-cm cells is from about 80 to 240 μg of vanadium per ml, and the sensitivity is 0.4 μg of vanadium per cm^2 at 740 mμ. The vanadium may be present initially as vanadium(IV) or vanadium(V), which is reduced to vanadium(IV) by the large excess of thiocyanate ion added. Several elements interfere in the determination; a separation procedure involving mercury cathode electrolysis is suggested.

RÉSUMÉ

Une méthode est décrite pour le dosage spectrophotométrique du vanadium, sous forme de thiocyanate de vanadium(IV) pyridine. Le complexe formé en solution acide est bleu et est extrait dans un mélange pyridine–chloroforme. Plusieurs éléments gènent; une méthode de séparation est proposée, par électrolyse avec cathode de mercure.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Vanadium. Der mit Thiocyanat und Pyridin gebildete blaue Komplex wird mit Pyridin–Chloroform extrahiert und die Absorption der Lösung gemessen. Die Entfernung störender Elemente erfolgt durch Elektrolyse mit einer Quecksilber-Kathode.

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CHLORPROMAZINE HYDROCHLORIDE AS AN ANALYTICAL REAGENT

PART II. COLORIMETRIC DETERMINATION OF MICRO QUANTITIES OF GOLD

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Most methods available for the colorimetric determination of gold depend on complex formation with organic compounds. Among suitable reagents are *p*-dimethylaminobenzylidene rhodanine[1–3], rhodamine B[4,5] and *o*-aminobenzene arsonic acid[6]. These methods are long and tedious, particularly when interfering ions are present. Very variable results are often obtained; this can be partly attributed to the difficulties encountered in stabilising the colours of the solutions.

Various organic substances are oxidized by auric salts to coloured products and this has also formed the basis of several methods for the determination of gold. *o*-Tolidine[7], *o*-dianisidine[8] and leuco malachite green[9] are some of the reagents that have been proposed.

It has been shown that gold oxidizes chlorpromazine hydrochloride in acid media to give a red coloured free radical which may be used for the detection of the element[10]. In the present investigation the use of chlorpromazine hydrochloride for the colorimetric determination of gold has been studied.

EXPERIMENTAL

Reagents

(*a*) Aqueous chlorpromazine hydrochloride solution: 50 mg/ml.

(*b*) Standard gold solution: Digest 50 mg of pure gold with 3 ml of concentrated nitric acid and 6 ml of concentrated hydrochloric acid for 1.5 h on a steam bath. Transfer to a 500-ml volumetric flask and dilute to the mark with water. This stock solution contains 100 μg of gold per ml. Prepare working solutions containing 10 μg, 20 μg and 40 μg of gold per ml by dilution as required.

Procedure

An aliquot of the standard gold solution was pipetted into a 25-ml volumetric flask and 10 ml of 50% (v/v) phosphoric acid and 3 ml of the reagent solution were added. The solution was diluted to volume with distilled water and the absorption was measured against distilled water after 30 min.

RESULTS AND DISCUSSIONS

The absorptions of the red coloured free radical against distilled water were measured with a Hilger spectrophotometer using cells of 1 cm path length and the values are plotted in Fig. 1. The absorption spectra shows a maximum at 530 mμ and all subsequent measurements were made at that wavelength.

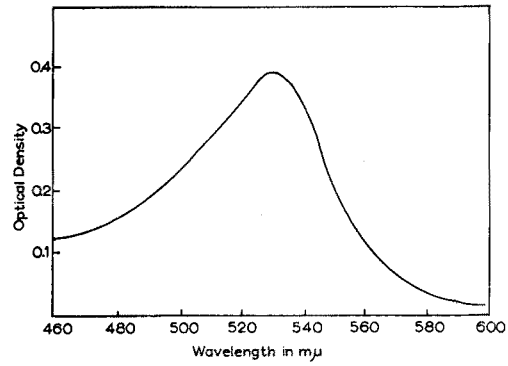

Fig. 1. Spectra of oxidized chlorpromazine hydrochloride in 20% phosphoric acid solution.

Effects of time, acid, and reagent concentrations

The absorption of the red coloured solution increased slightly with increasing acid and reagent concentrations (Fig. 2). When the acid and reagent concentrations were less than 15% (v/v) and 4 mg per ml respectively very variable results were obtained. The absorptions of such solutions decreased with decreasing acid and reagent concentrations. The colours of these solutions were not very stable. With sufficient excess of reagent the red colour was, however, independent of the reagent concentration. The optimum concentrations in the final solution were found to be 20% phosphoric

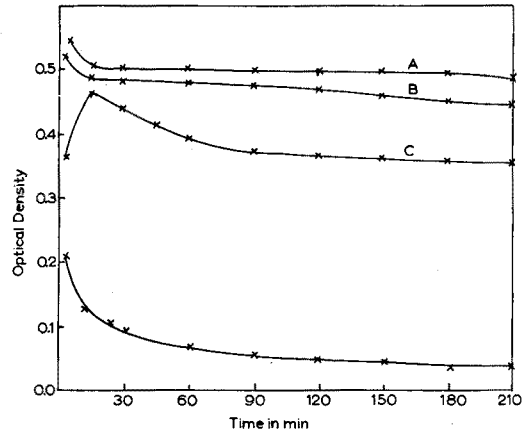

Fig. 2. Effects of time, acid and reagent concentrations. Au: 4 μg/ml. A: H_3PO_4, 20%; chlorpromazine hydrochloride, 6 mg/ml. B: H_3PO_4, 15%; chlorpromazine hydrochloride, 3 mg/ml. C: H_3PO_4, 8%; chlorpromazine hydrochloride, 1 mg/ml. D: H_3PO_4, 4%; chlorpromazine hydrochloride, 0.1 mg/ml.

acid and 5 mg of chlorpromazine hydrochloride per ml. The acid concentration could be raised to 35% without effect on the colour. Under the optimum conditions the colour of the free radical was found to be stable for at least 3 h and it remained unchanged under normal conditions of light and temperature (25–29°).

Beer's law

Different quantities of standard gold solution were mixed with 10 ml of 50% (v/v) phosphoric acid and 5 ml of chlorpromazine hydrochloride solution. The solutions were diluted to 25 ml so that the phosphoric acid concentration was 20% and the chlorpromazine hydrochloride concentration was 6 mg per ml in the final solution. The absorbances at 530 mμ were measured. The calibration curve was linear and Beer's law was obeyed over the range 0.5 to 8.0 μg of gold per ml of the final solution. Thus it is possible to determine 15 to 200 μg of gold by this method. The sensitivity of the method can be increased by decreasing the final volume from 25 ml to 10 ml. The results obtained were the same so long as the final acid concentration was 20% and the reagent concentration was not less than 5 mg per ml.

Reproducibility of results

Replicate determinations were carried out on samples giving 4 μg of gold per ml of the final solution. The following optical densities were observed: 0.545, 0.550, 0.552, 0.540, 0.554, 0.545, 0.560, 0.559; standard deviation 0.003.

Interference of foreign ions

The interference of a number of ions commonly associated with gold was investigated. The following caused no interference: Na, Mg, K, Ca, Cu, Ag, Fe, Hg, Co, Ni, Cd, Zn, Pb, As, Al, Mn, Cr, UO_2^{+2}.

Serious interferences were found with ions which either oxidized the reagent, *e.g.* ceric, dichromate, permanganate and vanadate, or ions which formed complexes with it, *e.g.* palladium and platinum. The complexes formed by palladium and platinum can, however, be removed by extraction with chloroform and an investigation is being made to find a suitable method for the determination of gold and these two metals in mixtures.

Stannous chloride, titanous chloride, sulphites and ascorbic acid interfere by reducing the auric ion or the red coloured free radical, thus bleaching its colour. EDTA also interferes by forming a complex with the gold. If any of these substances are present in the test solution they should be removed by fuming with aqua regia. Nitric acid of strength greater than 15% oxidizes chlorpromazine hydrochloride but weaker solutions have no effect. Iron cannot be totally suppressed with phosphoric acid if the chloride concentration of the final solution exceeds 1 *M*. The present method which recommends the use of phosphoric acid was specially adapted for the determination of gold in the presence of large amounts of iron. In the absence of iron *M* hydrochloric acid can be used in place of phosphoric acid.

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SUMMARY

Chlorpromazine hydrochloride is proposed for the colorimetric determination of gold in acidic medium at 530 mμ. Comparatively large amounts of copper, silver, iron, lead, etc. can be tolerated. The colour is stable; Beer's law is obeyed over the range 0.5–8 μg of gold per ml.

RÉSUMÉ

Le chlorhydrate de chloropromazine est proposé comme réactif pour le dosage colorimétrique de l'or en milieu acid, à 530 mμ. Ce dosage peut être effectué en présence de relativement fortes teneurs en cuivre, argent, fer, plomb.

ZUSAMMENFASSUNG

Zur colorimetrischen Bestimmung des Goldes wird Chloropromazinhydrochlorid als Reagenz vorgeschlagen. Die Gegenwart relativ grosser Mengen von Kupfer, Silber, Eisen und Blei stört nicht.

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SPECTROPHOTOMETRIC DETERMINATION OF CHROMIUM WITH 1,2-DIAMINOCYCLOHEXANETETRAACETIC ACID

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INTRODUCTION

1,2-Diaminocyclohexanetetraacetic acid (DCTA) forms very stable complexes with certain metals[1]. Some of these are coloured and consequently DCTA is used in colorimetric determinations of copper[2–4], manganese[5], iron[6–8] and cobalt [9,10]. Chromium gives a violet colour when boiled with DCTA. VERMA *et al.* have suggested the use of this colour reaction for the quantitative determination of trivalent chromium in presence of hexavalent chromium[11] and in presence of iron and small amounts of nickel[12].

The present paper describes the trivalent chromium–DCTA complex. The composition and stability of the complex have been determined and methods for the determination of chromium in presence of some other metals are given.

INSTRUMENTS AND REAGENTS

Apparatus

A Zeiss spectrophotometer model PMQ II with 1.000- and 5.000-cm glass cells was used for the determination of optical densities. The pH of all solutions was measured with a Beckman Zeromatic pH meter.

Reagents

All chemicals used were of reagent grade except for the 1,2-diaminocyclohexanetetraacetic acid which was a purum product obtained from Fluka.

A stock solution of chromium was prepared by dissolving 9.6 g of $KCr(SO_4)_2 \cdot 12\ H_2O$ in water and diluting to 1 l. The molarity was checked against DCTA (JOB's Curves) and found to contain 0.957 g of chromium per l or 0.0184 mol.

The DCTA stock solution was prepared by dissolving 17.336 g of 1,2-diaminocyclohexanetetraacetic acid and 4 g of sodium hydroxide in water and diluting to 500 ml. The molarity was checked by titration of a standard zinc solution using eriochrome black T as indicator and found to be 0.09414 *M*. Less concentrated standard solutions of the reagent were prepared by appropriate dilution.

An acetic acid/sodium acetate buffer was prepared by dissolving 68 g of $CH_3COONa \cdot 3\ H_2O$ and 30 ml of acetic acid ($d = 1.05$) in water and diluting to 1 l. The pH of this buffer was 4.65.

Stock solutions of copper, cobalt and nickel were prepared by dissolving the appropriate amounts of $CuSO_4 \cdot 5\ H_2O$, $Co(NO_3)_2 \cdot 6\ H_2O$ and $NiSO_4 \cdot 7\ H_2O$ in water and standardized by electrolysis.

EXPERIMENTAL

Absorption curve

An acid solution of chromium(III) and DCTA will give a violet complex. Fig. 1 shows the absorption curve which exhibits maxima at 395 and 540 mμ.

The complex is not formed immediately. The colour did not reach its maximum value even after a week at room temperature (Fig. 2). When the temperature was raised to 100° the complex was formed rapidly. The colour was fully developed after only 5 min of gentle boiling. Once formed, the complex seemed to be stable for months.

The colour intensity had its maximum value in the pH region 1.5 to 6.5. In this pH range the optical densities were fairly constant.

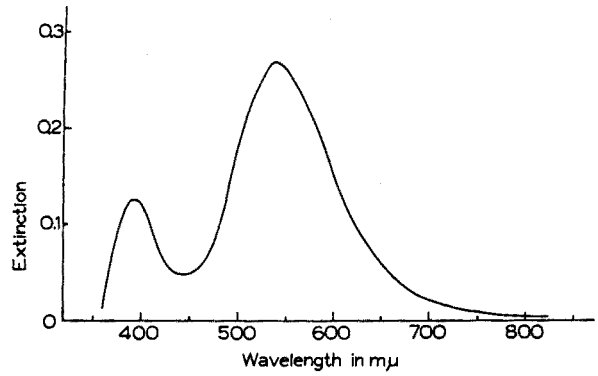

Fig. 1. Absorption curve of a $2.2 \cdot 10^{-4}$ *M* chromium complex with DCTA in acetate buffer of pH 4.65.

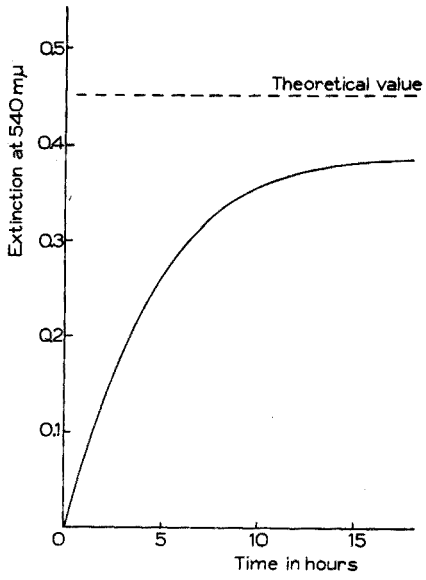

Fig. 2. The extinction of a solution, containing $3.68 \cdot 10^{-4}$ mol chromium and $9.4 \cdot 10^{-3}$ mol DCTA, plotted against the time elapsed from mixing the solution. The temperature was 20°.

Beer's law

For the verification of Beer's law the optical densities were measured for many chromium concentrations. An excess of DCTA was added to the chromium after the pH was adjusted to 4.65 by an acetic acid buffer. The solution was boiled gently for

5 min. After cooling to room temperature it was diluted to 100 ml. The absorption was measured at 540 mμ against distilled water as a blank. The absorption plotted against the chromium concentration gave a straight line passing through the origin. The system was found to obey Beer's law in the concentration range 2 to 150 μg chromium per ml.

The molar extinction coefficient of the chromium–DCTA complex was found to be 245.

Interfering ions

Provided that excess reagent is present, colourless ions do not interfere in the determination of chromium. Cobalt(III) and large amounts of copper and nickel contribute to the optical density at 540 mμ, but it is still possible to determine chromium in presence of these ions. The cobalt(III) complex has a maximum absorption at 545 mμ while the cobalt(II) complex gives nearly no absorption. A reduction to cobalt(II) thus makes it possible to determine the chromium content in a solution containing chromium and cobalt. The chromium and the copper complex have their maximum absorbances at different wavelengths and so can be determined. The nickel complex seems to be formed instantly while the chromium has to be boiled. If the absorption of a boiled solution is measured against a blank which is not boiled, the extinction is due to the chromium complex alone.

PROCEDURES

Chromium and copper

A solution containing chromium and copper may be analysed in the following way. The mixture is buffered, an excess of reagent is added and the solution is boiled for 5 min. After cooling to room temperature and diluting to a constant volume the extinctions are measured at 540 and 720 mμ.

In Table I some extinctions measured at 540 and 720 mμ are given. The theoretical absorbances were taken from standard curves. As seen from the table, copper and chromium may be determined in the same solution with an experimental error of about 2%.

Chromium and cobalt

A solution containing chromium and cobalt may be analysed in the following way. An aliquot is buffered, an excess of reagent and 30% hydrogen peroxide are added and the solution is boiled gently for 10 min. After cooling to room temperature it is diluted to a constant volume. The extinction is measured at 540 mμ. The optical density is due both to the cobalt(III) complex and the chromium complex. Another aliquot is treated in the same way, but with a reducing agent instead of the hydrogen peroxide. The extinction measured at 540 mμ is then due to the chromium complex alone. Both the chromium and cobalt concentration may be found from standard curves. Table I shows an example.

Chromium and nickel

A solution containing chromium and nickel may be analysed as follows. An aliquot is buffered, an excess of reagent is added and the mixture is boiled for 5 min. After cooling to room temperature it is diluted to a constant volume. The extinction is

TABLE I

PHOTOMETRIC DETERMINATION OF CHROMIUM IN PRESENCE OF COPPER, COBALT AND NICKEL

Molarity	E theoretical		E measured		Error (%)	
	720 mμ	540 mμ	720 mμ	540 mμ	720 mμ	540 mμ
$5.28 \cdot 10^{-4}$ *M* Cu	0.289	0.026	0.311	0.703	—1.6	—0.14
$5.52 \cdot 10^{-4}$ *M* Cr	0.027	0.678				
$7.92 \cdot 10^{-4}$ *M* Cu	0.433	0.038	0.440	0.264	—0.45	+0.76
$1.84 \cdot 10^{-4}$ *M* Cr	0.009	0.224				
$5.28 \cdot 10^{-4}$ *M* Cu	0.289	0.026	0.310	0.468	+0.98	—1.27
$3.68 \cdot 10^{-4}$ *M* Cr	0.018	0.448				
$3.50 \cdot 10^{-4}$ *M* Co(III)		0.520		0.978		+1.03
$3.68 \cdot 10^{-4}$ *M* Cr		0.448				
When boiled with a reducing agent:				0.459		+2.45
$3.40 \cdot 10^{-3}$ *M* Ni, $3.68 \cdot 10^{-4}$ *M* Cr, boiled		0.086 0.448		0.533		—0.19
$3.40 \cdot 10^{-3}$ *M* Ni, $3.68 \cdot 10^{-4}$ *M* Cr, not boiled		0.086 0.046		0.130		—1.52

measured at 540 mμ against an aliquot treated in the same way, but not boiled (this solution must be prepared immediately before) and against distilled water. In the first case the absorption is due to the chromium complex alone, in the second case it is due to both the chromium and nickel complexes. The chromium and nickel content may be found from standard curves. Table I shows an example.

The composition of the chromium complex

DCTA usually forms 1:1 complexes with metals. JOB's method of continuous variation[13] shows that one mole of DCTA will also combine with one mole of chromium. The same maximum occurs at different wavelengths (500, 540 and 600 mμ) indicating that only one coloured complex exists at pH 4.65.

Since $Cr(H_2O)_6^{+3}$ is violet and DCTA is polydentate, the complex can be assumed to be either $[CrR]^-$ or $CrRX_2$ where R is DCTA and X is H_2O, OH^- or CH_3COO^-. In alkaline medium the extinction at 540 mμ decreases and the absorption maximum is displaced to 590 mμ. This is probably due to the formation of chromium hydroxide before boiling and the entrance of OH-groups in the complex.

The stability of the chromium complex

Preliminary experiments showed that the stability of the chromium– and copper–DCTA complexes are of the same order.

Chromium(III) and copper ions form 1:1 complexes with DCTA and the concentration of these two chelates can be determined in presence of each other. The stability constant of the copper chelate has been determined previously[1]. Consequently the same displacement method used by JACOBSEN AND SELMER-OLSEN[10] may be used in the calculation of the stability of the chromium complex.

Solutions containing chromium, buffer and a slight excess of reagent were boiled for 5 min. After the solutions were cooled to 20°, a known amount of copper was added and the solutions were diluted to 100 ml. The absorption was measured against distilled water at 540 and 720 mμ. An equilibrium was indicated by constant ex-

tinctions. The concentrations of metal complexes, uncomplexed metals and the stability constant were calculated. The results are given in Table II. All measurements were made at 20° in solutions of ionic strength 0.1. A mean value of the stability constant $K_{CrR} = 1.9 \cdot 10^{22}$ was obtained when the value of log K_{CuR} was taken as equal to 21.30[1].

TABLE II

DETERMINATION OF THE STABILITY CONSTANT OF CHROMIUM–DCTA

Total molar concentration·10⁴		*Extinction measured*		*Molar concentration found·10⁴*				log K_{CrR}
Cr	*Cu*	*720 mμ*	*540 mμ*	*CuR*	Cu^{+2}	*CrR*	Cr^{+3}	
8.28	1.76	0.092	0.793	0.87	0.89	6.24	2.04	21.8
8.28	4.40	0.122	0.807	0.93	3.47	6.34	1.94	22.4
8.28	5.28	0.141	0.817	1.11	4.17	6.93	1.35	22.6
							Mean	22.27

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SUMMARY

Chromium(III) forms a water-soluble complex with DCTA. The violet complex has maximum absorbance at 540 mμ and obeys Beer's law from 2 to 150 μg chromium per ml. The molar extinction coefficient is 245. Determinations of copper and chromium, cobalt and chromium, and nickel and chromium in presence of each other are described. The complex contains chromium and the reagent in a ratio of 1 : 1. The stability constant of the complex is $1.9 \cdot 10^{22}$.

RÉSUMÉ

Une méthode est décrite pour le dosage spectrophotométrique du chrome au moyen de l'acide diamino-1,2-cyclohexanetétracétique. On obtient un complexe violet avec maximum d'absorption à 540 mμ. Des procédés sont donnés pour effectuer ce dosage en présence de cuivre, de cobalt ou de nickel.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Chrom mit Hilfe von 1,2-Diaminocyclohexantetra-essigsäure. Das Absorptionsmaximum des gebildeten violetten Komplexes liegt bei 540 mμ. Es werden ferner Verfahren beschrieben zur gleichzeitigen Bestimmung von Chrom und Kupfer, Kobalt oder Nickel.

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THE REACTION OF THORIUM WITH 1-(1-HYDROXY-4-METHYL-2-PHENYLAZO)-2-NAPHTHOL-4-SULFONIC ACID IN PRESENCE OF EDTA AND ITS APPLICATION IN THE SPECTROPHOTOMETRIC DETERMINATION OF THORIUM IN URINE*

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INTRODUCTION

LINDSTROM AND DIEHL[1] in their search for an indicator more stable than Eriochrome Black T synthesized 1-(1-hydroxy-4- methyl-2- phenylazo)-2-naphthol-4-sulfonic acid. They found this new indicator, which they trivially named Calmagite, to be superior to Eriochrome Black T in the titration of calcium and magnesium with (ethylenedinitrilo) tetraacetic acid (EDTA). Calmagite solutions were stable after one year, and the color change was reported to be clearer and sharper than that of Eriochrome Black T.

LOTT, CHENG AND KWAN[2] based a spectrophotometric determination of thorium on the fact that thorium forms a red colored complex with Eriochrome Black T, in the presence of certain masking agents, which were used to prevent foreign ion interference. They reported, however, some polyvalent ions, notably iron, interfered and had to be removed.

The determination of thorium in urine has been of recent interest. KIRBY AND BRODBECK[3] stated that radium-226, actinium-227, and thorium-228 may occur in the urine of laboratory workers who process neutron-irradiated radium-226. Various procedures for the determination of thorium in urine have been published[4,5]. These are generally lengthy and time-consuming partly because of the method for the destruction of urine and for the actual thorium determination.

Preliminary tests showed that Calmagite formed a red chelate complex with a number of metals at pH 10, and that masking agents could be used to displace the cation from the chelate complex except in the case of thorium. Consequently, it was decided to investigate the possibility of employing Calmagite as a color-forming reagent in the spectrophotometric determination of thorium and its use in the detection of thorium in human urine.

Information is reported on the apparent stability constant of the thorium–Cal-

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magite complex, the stoichiometry of the reaction, and the optimum conditions for the spectrophotometric analysis of thorium in urine with Calmagite.

EXPERIMENTAL

Apparatus and reagents

The pH measurements were performed with a Beckman Model G pH Meter (Beckman Instruments, Inc., Fullerton, Calif., U.S.A.).

The absorbancies were obtained using a Beckman DU Spectrophotometer with water as the reference standard.

The Calmagite was obtained from the G. Frederick Smith Chemical Company of Columbus, Ohio, U.S.A., and stated by them to be of reagent grade purity. The compound was further purified according to the method given by LINDSTROM AND DIEHL[1].

An infrared spectrum was run on the Calmagite as received, on the acetone soluble fraction and on the acetone insoluble fraction, as obtained from the purification procedure, using the potassium bromide pellet technique. No significant difference between any of the fractions was noted.

A 0.005 *M* aqueous solution of Calmagite was prepared by transferring 0.4479 g of the acetone-soluble fraction (which is stated to be the purer form of the dye) to a 250-ml volumetric flask and diluting to volume. Other solutions were prepared by appropriate dilution.

Eriochrome Black T, 0.005 *M*, was prepared by dissolving 0.2197 g in methanol and diluting to 100 ml.

An aqueous solution of 0.1 *M* EDTA was prepared by dissolving 37.27 g of the disodium salt of (ethylenedinitrilo)tetraacetic acid in a 1-l volumetric flask and diluting to volume. The solution was standardized against reagent grade zinc[6]. The EDTA solution was adjusted to be 0.1000 *M*; the other EDTA solutions were prepared by the proper dilution of this solution.

The pH 10 buffer and the pH 8.5 buffer solutions were prepared as described previously[2].

Standard thorium solution was prepared by dissolving 3.181 g of reagent grade thorium perchlorate in water and diluting to 1 l. The solution was standardized by titration with 0.1000 *M* EDTA using xylenol orange indicator, and adjustments were made until it was 0.005000 *M* in thorium. Other thorium solutions were prepared by appropriate dilution of this solution.

Solutions for the qualitative determination of foreign ion interference were made by dissolving the appropriate amount of reagent grade chemical in 1 l of water containing about 1 ml of the concentrated acid of the salt's anion.

Qualitative tests

Qualitative tests were performed to determine the procedure which would give the least amount of foreign ion interference. For the tests listed in the first column of Table I, the following procedure was employed. To 2 ml of water in a test tube were added 2 drops of 0.01 *M* foreign ion solution, 2 drops of 0.1 *M* EDTA, 4 drops of 0.005 *M* Calmagite and 1 ml of pH 10 buffer. For the tests listed in the second column of Table I essentially the same procedure was employed except that 2 drops of aqueous 0.1 *M* hydroxylamine hydrochloride were added before the addition of EDTA.

TABLE I

COLORS OF IONS WITH CALMAGITE AT pH 10 AND AMOUNT OF FOREIGN ION INTERFERENCE

(at thorium concentration $1.3 \cdot 10^{-6}$ *M*)

Ion	*Dye and EDTA*	*Dye, hydroxylamine and EDTA*	*Absorbancy*[a] *640 mμ*
None	Blue	Blue	0.71
Al(III)	Blue	Blue	0.56
Ba(II)	Blue	Blue	0.70
Bi(III)	Blue	Blue	0.66
Ca(II)	Blue	Blue	0.60
Cd(II)	Blue	Blue	0.68
Ce(IV)	Blue[b]	Blue[b]	0.65
Co(II)	Blue[c]	Blue	0.51
Cr(III)	Blue	Blue	0.75
Cu(II)	Blue	Blue	0.66
$FeCl_3$	Blue[b]	Blue[b]	—
$Fe(NO_3)_3$	Blue[b]	Blue[b]	—
$Fe_2(SO_4)_3$	Blue[b]	Blue[b]	0.27[d]
$FeSO_4$	Blue[b]	Blue[b]	0.25
Hg(II)	Blue	Blue	0.73
La(III)	Blue	Blue	0.69
Mg(II)	Blue	Blue	0.68
Mn(II)	Blue	Blue	0.79
Ni(II)	Blue	Blue	0.67
Pb(II)	Blue	Blue	0.77
Sb(III)	Blue	Blue	0.75
Sn(II)	Blue-purple	Blue	0.71
Sn(IV)	Blue	Blue	0.74
Sr(II)	Blue	Blue	0.72
Th(IV)	Red	Red	—
Ti(IV)	Purple	Blue[c]	0.40[d]
U(IV)	Purple	Red	—
Zn(II)	Blue	Blue	0.72
Zr(IV)	Blue-purple	Blue	0.17[d]

[a] Foreign ion concentration $1 \cdot 10^{-5}$ *M*

[b] To brown in 2 min.

[c] To purple in 15 min.

[d] At a foreign ion concentration of $1.3 \cdot 10^{-6}$ *M*, absorbancies are: Ti(IV) 0.68; Fe(III) 0.63; Zr(IV) 0.63; U(IV) 0.60.

Spectrum, effect of pH, and estimation of foreign ion interference

The spectrum of the thorium–dye complex, as well as that of the dye alone, were determined using the procedure described below, except that no foreign ions were added to the solution; and, in the case of the dye only, no thorium was added. The spectra are reported in Fig. 1. Varying the pH of the above solutions, showed that the maximum difference in color intensity occurred at pH 10, as shown in Fig. 2.

For the estimation of the concentration of foreign ion that could be tolerated in the presence of thorium without appreciable interference, the following procedure was used. To a 50-ml volumetric flask, 6.0 ml of $1.077 \cdot 10^{-4}$ *M* thorium, 0.5 ml of 0.01 *M* foreign ion, 1.0 ml of aqueous 0.1 *M* hydroxylamine hydrochloride, 2.5 ml of 0.1 *M*

EDTA, 2.5 ml of 0.0025 *M* Calmagite, and 4.0 ml of pH 10 buffer were added. Then the absorbancy was determined within 5 min at 640 mμ. The third column of Table I lists the results so obtained.

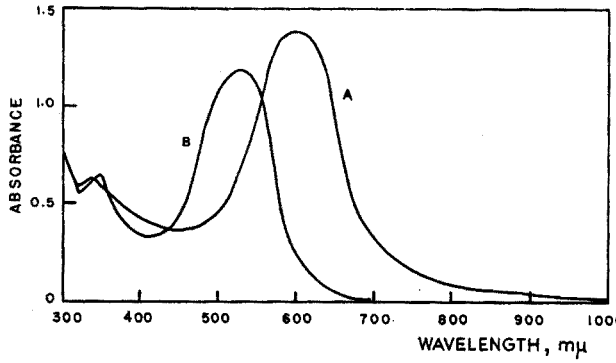

Fig. 1. Absorption curves A. Calmagite. B. Thorium–Calmagite complex.

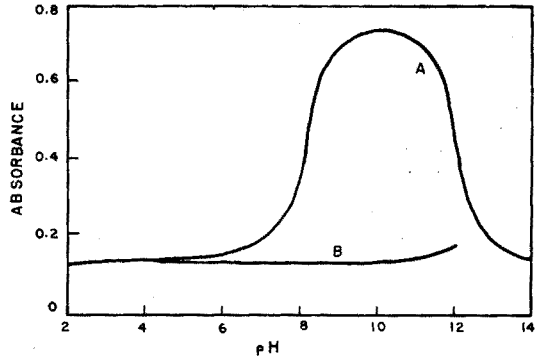

Fig. 2. Effect of pH. A. Calmagite at 610 mμ. B. Thorium–Calmagite complex at 610 mμ.

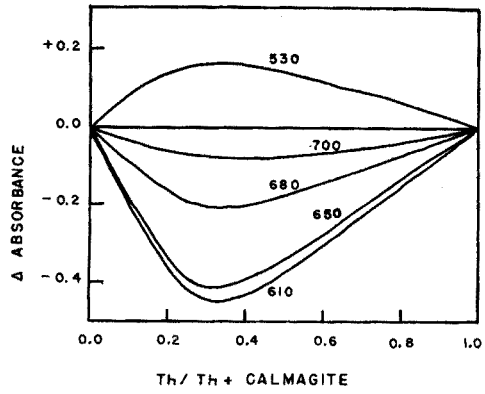

Fig. 3. Continuous variation study.

Method of continuous variations

The formula and stability constant of the thorium complex were determined by the method of continuous variations. To each of ten 100-ml volumetric flasks respectively 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0 ml of 0.00250 *M* thorium perchlorate were added, and 1.0 ml of 0.05 *M* EDTA. Next, to each flask, in the same order respectively 10.0, 9.0, 8.0, 7.0, 6.0, 5.0, 4.0, 3.0, 2.0, 1.0 and 0.0 ml of 0.00250 *M* Calmagite and 2.5 ml of pH 8.5 buffer were added. The flasks were brought up to volume with water. Absorbancies were measured at 700, 680, 650, 610 and 530 mμ.

Fig. 3 shows the results obtained when the absorbancy difference is plotted against composition. The data may be found in the thesis of P. J. CURCIO.

The same procedure was employed with 0.00125 *M* thorium perchlorate and 0.00125 *M* Calmagite solutions. In all cases, a complex composed of one part thorium to two parts Calmagite, was found to be formed.

Detection of thorium in human urine

Standard amounts of thorium were added to human urine. Preliminary tests showed that the direct determination of thorium in urine by the addition of Calmagite to samples at pH 10 was unsuccessful. However, if the thorium-containing samples of urine were decomposed before the addition of Calmagite, the analysis was possible.

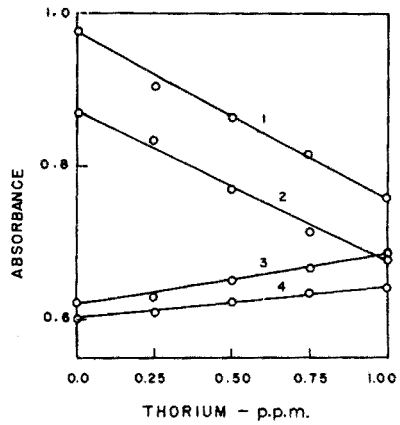

Fig. 4. Calibration curves. 1. Thorium in aqueous solution; 640 mμ. 2. Thorium in urine samples; 640 mμ. 3. Thorium in aqueous solution; 530 mμ. 4. Thorium in urine samples; 530 mμ.

The wet oxidation of urine was performed in the following manner. To a 150-ml beaker, 25 ml of urine containing thorium, 15 ml of concentrated nitric acid, 2.0 ml of 72% perchloric acid and 1.0 ml of sulfuric acid were added. The solution was heated on a hot plate. As fuming began, there was some frothing but no charring; the solution color was of a pale straw color. As the fuming continued the solution became colorless. The heating was continued until gaseous evolution ceased. During the later stages of heating, there was condensation on the beaker's inner surface. After the solution became colorless, heating was continued for an additional 5 min. On cooling, about 1.0 ml of a colorless clear solution remained; 20.0 ml of water was added,

followed by the addition of 2.5 ml of 0.1 *M* EDTA, 6 drops of 50% aqueous sodium hydroxide, 2.5 ml of 0.00250 *M* Calmagite and 3.0 ml of pH 10 buffer. The solution was transferred to a 50-ml volumetric flask and diluted to volume with water. The digestion procedure required about 1 h. In samples in which thorium was absent, Calmagite indicator remained in the unchelated "blue" form; in the thorium-containing samples the red colored complex formed.

Calibration curve for the thorium–Calmagite complex in "urine"

A calibration curve was constructed using known additions of thorium to urine. To each of eight 150-ml beakers was added respectively 0.0, 1.0, 2.0, 3.0, 4.0, 5.0, 7.0 and 10.0 ml of a solution containing 0.025 mg of thorium per ml. Then 25 ml of urine, 15 ml of concentrated nitric acid, 2.0 ml of 72% perchloric acid, and 1.0 ml of concentrated sulfuric acid were added to each beaker. The mixtures were digested following the wet oxidation procedure just described. For comparative purposes, a second calibration curve for the determination of thorium in aqueous solutions was prepared by the procedure described above except no urine was added to the samples. The calibration curves are presented in Fig. 4.

DISCUSSION

Aqueous solutions of Calmagite are blue in color at pH 10. With many di- and trivalent cations, Calmagite reacts at this pH to form a red chelate complex. If a second complexing agent is added which displaces the metal ion from the Calmagite complex, the solution turns blue. If the second complexing agent does not displace the metal ion, then the red color remains, which indicates that a stronger bond exists between the metal ion and the Calmagite than between the metal ion and the second chelating agent.

When EDTA, Calmagite and pH 10 buffer are added in that order to solutions of the cations listed in Table I, cerium(IV), iron(II) and iron(III) went from blue to brown in 2 min. Cobalt(II), tin(II), and zirconium(IV) went from blue to purple. Titanium(IV) and uranium(IV) went from red to purple. Thorium(IV) remained red.

When hydroxylamine hydrochloride was added before the EDTA, Calmagite and pH 10 buffer, the iron(II) and iron(III) changed from blue to brown in 2 min. Titanium (IV) went from blue to purple in 3 min. Cobalt(II), tin(II) and zirconium(IV) solutions remained blue. Thorium(IV) and uranium(IV) remained red. The hydroxylamine hydrochloride addition resulted in less interference.

No difference in iron interference was observed when iron was in the ferrous or ferric state. It made no difference in the interference due to iron, as well as the reaction of thorium, whether the anion was the chloride, nitrate, sulfate or phosphate. In addition, the interference was still evident when the following media were used in lieu of water; ethyl alcohol, acetone, or formaldehyde. Neither did the raising of the solution temperature have any effect. The following chelating agents were used instead of EDTA to attempt to eliminate ion interference, but without success: triethanolamine, tetraethylenepentaamine, tetraethylenetetraamine, triethylenetetraamine sulfate, diethylenetriamine pentaacetic acid, 1,2-diaminocyclohexanetetraacetic acid and hydroxethylethylenediamine triacetic acid. The last two were obtained from the Geigy Chemical Corporation, Ardsley, N.Y., U.S.A. The above listed chelating agents however, did not affect the reaction of thorium with Calmagite.

Calmagite and Eriochrome Black T experience the same interference. Using data presented primarily for Eriochrome Black T[2], it would be assumed that the following ions would not cause interference: gadolinium(III), praseodymium(III), samarium(III), ytterbium(III), dysprosium(III), erbium(III), europium(III), holmium(III), lutetium(III), and thulium(III).

Quantitatively it was found that at a molar ratio of 7.75 of foreign ion to thorium, of the foreign ions listed in Table II, only aluminum(III), cobalt(II), iron(II), iron(III) titanium(IV), and zirconium(IV) interfered by an appreciable lowering of the absorbancy. When the molar ratio was lowered one to one, then uranium(IV), iron(II), iron(III), and zirconium(IV) interfered slightly.

A continuous variation study at pH 8.5 showed the formation of one complex. Representing Calmagite by HD^{-2}, then based upon the continuous variation study, the reaction would be:

$$Th^{+4} + 2\,HD^{-2} \rightarrow ThD_2^{-2} + 2\,H^+$$

The apparent stability constant was found to be $2.4 \cdot 10^8$, using two different procedures[7,8]. A pH of 8.5 was chosen for this study to lessen the possibility of the formation of polynuclear complexes through hydroxo bridges[9,10]. The linearity of the calibration curves at 640 mμ, indicates that no appreciable amount of a second complex is formed at pH 10.

The procedure for analysis of thorium in urine developed in this paper was found to be shorter and more sensitive. The sensitivity of the procedure of PERKINS AND KALKWARF is 0.03 to 0.04 μg per square cm per 0.001 absorbance unit[4]. The sensitivity of the procedure described in this paper is 20 times greater; 0.008 μg per square cm per 0.001 absorbance unit at 640 mμ.

Examination of Fig. 4 shows that the absorbancies of thorium in urine are lower than those found for thorium in aqueous solution. This may be due to the presence of trace amounts of foreign ions in urine which lower the absorbancy slightly and to the incomplete oxidation of the urine. The constituents appear to be constant in the urine samples tested, as reproducible results were obtained with the same calibration curve over a period of time. The accuracy for the determination of thorium in urine samples was found to be $\pm 4\%$ of the amount of thorium present in the sample.

SUMMARY

1-(1-Hydroxy-4-methyl-2-phenylazo)-2-naphthol-4-sulfonic acid (Calmagite) can be used for the spectrophotometric determination of thorium in urine, by employing EDTA and hydroxylamine as masking agents. By the method of continuous variations, it was found that two moles of Calmagite reacted with one mole of thorium, and that the apparent stability constant was $2.4 \cdot 10^8$ at pH 8.5. A procedure was developed for the rapid wet oxidation of urine, using a mixture of nitric, perchloric and sulfuric acids. The sensitivity of the reaction for thorium was found to be 0.008 μg per square cm per 0.001 absorption unit at 640 mμ. The molar absorptivity of the thorium complex was found to be 53000 at 640 mμ at pH 10.0.

RÉSUMÉ

Une méthode est décrite pour le dosage du thorium dans l'urine par spectrophotométrie, en utilisant comme réactif l'acide 1-(1-hydroxy-4-méthyl-2-phénylazo)-2-naphtol-4-sulfonique (Calmagite), et comme agents de masquage, EDTA et hydroxylamine. D'autre part, un procédé a été mis au point pour la décomposition rapide de l'urine, par voie humide, en employant un mélange d'acides nitrique, perchlorique et sulfurique.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Methode zur Bestimmung von Thorium in Urin mit 1-(1-Hydroxy-4-methyl-2-phenylazo)-2-naphtol-4-sulfosäure als Reagenz und EDTA und Hydroxylamin als Maskierungsmittel. Zur raschen Zersetzung des Urins wird ein Gemisch von Salpetersäure, Perchlorsäure und Schwefelsäure verwendet.

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Short Communications

A spectrophotometric assay of water in organic solvents

In studies on the use of chloranilic acid as a reagent in paper chromatography[1] it was found that the presence of small amounts of water in the solvent gave rise to purple tinges, quite different from the usual brownish color of the organic solutions of the reagent. This led us to study the use of chloranilic acid for the assay of water in organic solvents. KOLTHOFF[2] suggested a method for the assay of water in ethanol which depends on the fact that the sensitivity of methyl orange to acid decreases with increasing concentrations of ethanol. The present method is more accurate and more convenient in use.

Chloranilic acid dissolved in ethanol shows an absorbance maximum at 460 mμ; in aqueous solutions the maximum is found at 535 mμ. For the assay of water, under the conditions described below, the best results were found by measuring the extinction at 520 mμ, because the absorbance maxima are displaced towards smaller values, as shown in Fig. 1.

Reagent

Chloranilic acid was used as a 2 m*M* solution in absolute ethanol (Merck Darmstadt), the reagent is stable when kept in a well-stoppered dark bottle in a refrigerator.

Procedure

A 1 ml sample of the water-containing organic solvent was added to 9 ml of absolute ethanol. A 5 ml aliquot of the mixture was then added to 5 ml of the chloranilic acid

reagent, and the extinction was read at 520 mμ, against a blank containing 5 ml of absolute ethanol and 5 ml of the reagent. The use of such a blank makes the dehydration of the ethanol used in the assay unnecessary.

The final readings were obtained as percentage values, found from a straight-line standard curve drawn between zero and 100% water in the sample (samples consisting of water plus absolute ethanol).

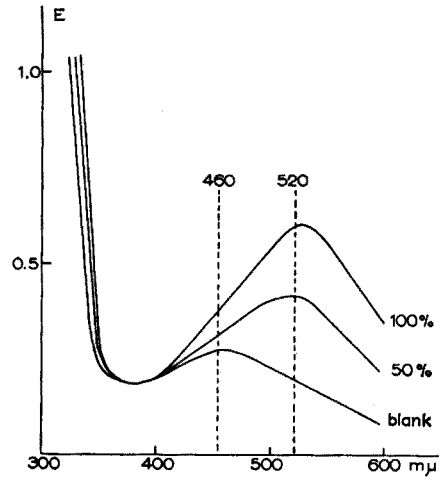

Fig. 1. Absorption spectra of a 1 m*M* chloranilic acid solution in absolute ethanol (blank) and in the presence of samples containing 50% and 100% water, assayed as described.

The maximum deviation found for the results was 2.5%, the relative mean deviation being 1.5%. The limit of sensitivity was found to be 2% of water in the sample. The color formed is stable for many hours, provided that the reaction vessels are well-stoppered and stored in a refrigerator.

The method as described cannot be used for the assay of water in nitrogen-containing solvents, such as pyridine, because they react with chloranilic acid[3].

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A modified isopiestic method for the micro-determination of molecular weights

In an earlier publication[1] a method was described for the micro-determination of molecular weights of organic compounds by the isopiestic method with simple laboratory apparatus. Since that time, it has been found that a refined version of the original apparatus allows a more rapid attainment of equilibrium. Moreover, if two standard substances are placed in the apparatus during each determination a check on the attainment of equilibrium can be obtained by calculating the molecular weight of one using the other as standard.

Two different designs of apparatus are available for isopiestic molecular weight determinations. In the H-shaped apparatus of CLARK[2], modified by CHILDS[3], the sample and standard substance are equilibrated with solvent in one position and the quantity of solvent associated with each is measured volumetrically by inverting the apparatus so that the solutions run into narrow calibrated measuring tubes. The other, which is described here, is a modification of SINCLAIR's method[4] for the determination of activity coefficients, in which the sample and standard substance are contained in separate vessels inside a larger one and the quantity of solvent associated with each is determined by weighing.

Isopiestic methods compare favourably with other methods; the sample is easily recovered at the end of the experiment, a wide range of solvents may be used, and the relatively low temperatures required make it suitable for many thermally unstable compounds. Although isopiestic methods are slow compared to thermistor methods[5], they require very little attention apart from initial weighing of samples and the measurement of the weight or volume of solvent associated with each at intervals of about 24 h. The apparatus required is inexpensive.

APPARATUS AND PROCEDURE

After preliminary experiments had been made on the rate of attainment of equilibrium under various conditions, the modified apparatus was reduced in volume so that the amount of free space was a minimum. The solutions are as close together as possible and provision is made for adequate thermal conduction between them. Adequate agitation of the solutions is provided by rotation, and the apparatus is capable of evacuation and of retaining a partial vacuum during the determination.

The apparatus (Fig. 1) is made from two similar thick-walled Petri dishes of 35 mm diameter which fit together at a ground surface. The upper half is fitted with an exit tube and stopcock to allow evacuation. The four platinum crucibles (1.3 ml capacity) are contained in the lower half. They rest on a copper block and fit into holes in a coiled strip of copper sheet. A further broad strip of thin copper sheet surrounds the group of four crucibles to prevent them from coming in contact with lubricant from the ground joint.

When the apparatus is closed during a determination the ground butt joint is lightly coated with silicone grease. A broad rubber band surrounds the joint and the two halves are clamped together by a metal clamp. The whole apparatus is enclosed in a watertight polythene bag and immersed in a thermostat, which can be adjusted to different temperatures for various solvents. The apparatus is rotated (30 r.p.m.)

at an angle of 10° by fitting it into a slipjoint on the drive shaft of a motor fitted with reduction gears.

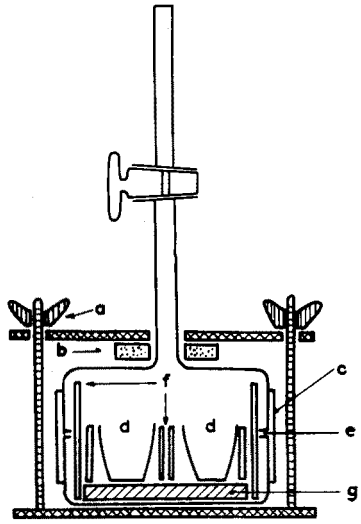

Fig. 1. Modified apparatus for isopiestic method. a. Metal clamp; b. rubber cushion; c. rubber band; d. platinum crucibles (2 shown); e. ground butt joint; f. copper sheet; g. copper block.

Samples of 3–10 mg are weighed into two of the platinum crucibles and standard substances into the other two. Each crucible is then weighed inside a weighing bottle with a carefully ground stopper, on a rapid semimicro balance. The procedure is then similar to that previously described[1] except that only about 0.25 ml of free solvent is allowed to flow over the copper block in the base of the apparatus before it is closed. With solvents of relatively low volatility the evacuation process should be repeated a second time after an interval of about 5 min. The attainment of equilibrium, which normally takes 48 h, is checked by calculating the molecular weight of one standard with respect to the other. However, it is advisable to continue until two consecutive readings at 24-h intervals give a constant value.

RESULTS AND DISCUSSION

Typical results are shown in Table I. Erroneous results caused by differences in activities between sample and reference solutions are overcome by a careful choice of solvent and, where possible, by employing a reference substance with a similar structure or properties to those of the test substance. The choice of solvent is important. Chloroform can be used extensively because it dissolves a wide range of compounds and is very volatile, thus giving high equilibration rates. For some compounds, however, chloroform promotes side effects which preclude a successful determination. For example, the molecular weight of benzoic acid in chloroform was found to be 175, which indicates partial association, but in acetone it was 126 (theoretical value, 122).

The effect of temperature on the rate of equilibration was found to be considerable. A constant temperature is important during each determination but this temperature should be varied according to the volatility of the solvent used. For example benzene,

TABLE I

RESULTS OBTAINED

Compound[a]	Weight (mg)	Solvent	Temp. (°C)	Molecular weight	
				Found	Theoretical
Atropine	4.783	Chloroform	40	295	289
Azobenzene (m.w. 182)	4.854				
o-Iodobenzoic acid	4.896	Chloroform	40	240	248
Azobenzene (m.w. 182)	5.089				
Salicylic acid	8.003	Acetone	40	135	138
Phenacetin (m.w. 179)	6.413				
Phenyl benzoate	4.426	Acetone	40	197	198
Azobenzene (m.w. 182)	4.190				
Pyrene	5.781	Benzene	60	202	202
Anthracene (m.w. 178)	5.453				
2,3-Dimethylnaphthalene	5.195	Benzene	60	160	156
Anthracene (m.w. 178)	5.453				

[a] The second compound in each pair was used as the reference substance.

a suitable solvent for polycyclic aromatic hydrocarbons, gives very slow equilibration rates at 40° but at 60° the rate is quite rapid. Ethanol with its high latent heat of vaporisation gives a very slow equilibration rate even at 60°.

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A sensitive test for nitrate

In the detection of nitrate, the ion is generally reduced to nitrite or ammonia because the characteristic reactions of nitrate itself are not sufficiently selective. Many tests

for nitrite or ammonia are selective or even specific and are often very sensitive. This last point is of interest, because the reduction of nitrate is seldom quantitative. However, a very sensitive reagent can be readily spoiled by traces of ammonia and nitric oxides from the atmosphere, and blank tests are nearly always positive.

An almost quantitative conversion of nitrogen(V) to nitrogen(III) is achieved by the formation of nitrosyl chloride from nitrate and gaseous hydrogen chloride:

$$HNO_3 + 3HCl \rightarrow NOCl + Cl_2 + 2H_2O$$

When concentrated sulphuric acid reacts with a mixture of sodium chloride and a nitrate gaseous nitrosyl chloride is formed; the latter can be made to react, either immediately or after hydrolysis to nitrous acid, with a suitable aromatic amine. The product of this diazotization can be converted to a dye by coupling with other compounds.

If sulphanilic acid and 8-hydroxyquinoline respectively are used for the diazotization and the coupling, the reaction is positive even when only 1 μg of nitrate is present; both reagents keep well in solution.

Procedure

Ignite a porcelain crucible (20 × 20 mm) to remove traces of nitrate and acids (in the presence of acids the nitrate would evaporate as nitric acid during the next operation). Place 1 drop of the neutral or weakly alkaline test solution, or a few mg of the solid with 1 drop of water, in the crucible. Add approximately 5 mg of sodium chloride, evaporate to dryness and then heat slowly until decrepitation begins. After cooling, add 1 drop of concentrated sulphuric acid (p.a.) and cover the crucible with a piece of filter paper moistened with reagent I (see below). If nitrate is present a brownish orange ring appears on the paper.

The limit of identification is rather less than 1 μg.

Oxidants which liberate chlorine from sodium chloride, and thus cause a coloration, must be absent; other interferences are thiosulphate, sulphite, thiocyanate and iodide, and any compounds which reduce the concentrated sulphuric acid to sulphur dioxide. Naturally nitrite must be absent.

If a more sensitive test is necessary, notwithstanding the drawbacks, the following procedure can be used to identify still smaller amounts of nitrate.

Just before the experiment is started, place a piece of ashless filter paper (SCHLEICHER AND SCHÜLL 589(1); 20 × 20 mm) that has been boiled with water to remove adsorbed nitric oxides and then stored under water, on a glass slide (25 × 25 mm); remove the excess of the water by blotting the edges with filter paper.

Place 1 drop of freshly prepared reagent II on the paper and cover with a second glass slide to protect it from atmospheric contamination. After a few minutes, remove the upper glass slide and blot the edges of the paper until it is only just moist. Then invert the slide with the paper and place it on a crucible (10 × 10 mm) prepared as described above. In this case the sodium chloride must be previously ignited to remove traces of nitrate and nitrite. After addition of 1 drop of concentrated sulphuric acid (p.a.) a pink colour is formed after 5 min; this is best observed by placing the paper on a white background.

The limit of identification is 3–5 ng.

Reagents

I: 20 mg sulphanilic acid, 5 mg 8-hydroxyquinoline, 1 g sodium acetate, and 5 ml water.

II: 15 mg sulphanilic acid, 3 mg N-ethyl-α-naphthylamine-hydrochloric acid, 2 g sodium acetate, and 5 ml water.

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Book Review

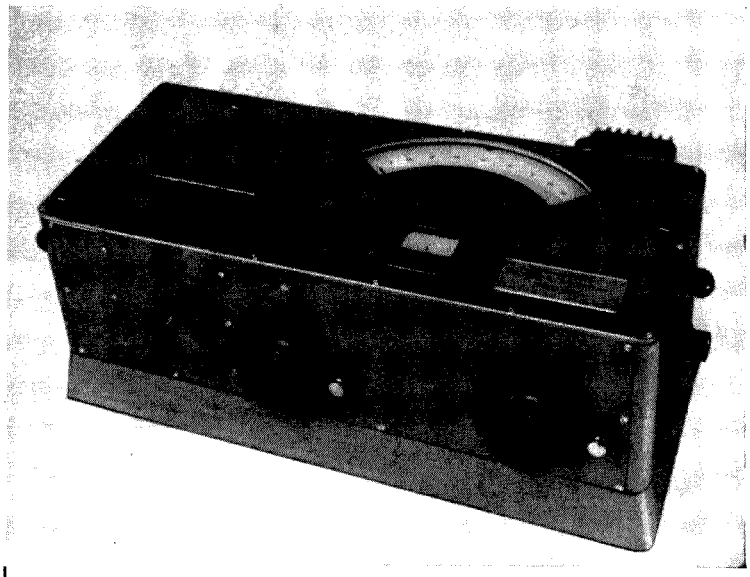
Methods for the Analysis of Non-soapy Detergent (NSD) Products, by G. F. LONGMAN and J. HILTON, The Society for Analytical Chemistry, London, 1961, Monograph No. 1, 30 pp., 15s.

This monograph is the first of a series dealing with specialised aspects of industrial analysis and gives full details for the isolation of the components commonly found in commercial detergents, namely, non-detergent organic material, organic detergent, lather improvers, fluorescent agents, inorganic bleaches, builders and water softening agents.

The chapters deal with the isolation by solvent extraction of the different components, and the methods used in the determination and identification of the organic active material. A classification of the commoner types of active material is given together with tables which enable the analyst to identify the members of each class of detergent. The determination of the inorganic materials and fluorescent agents is dealt with in the final chapter.

The monograph is of particular interest to the analyst who does not work in the detergent industry but is however occasionally confronted with such analyses. Though only eleven references are given, the first two lead to a very adequate coverage of the literature up to 1959. This would certainly form an excellent introduction to the field of detergent analysis.

W. R. STONE (London)



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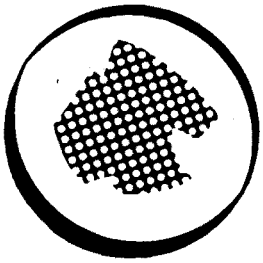

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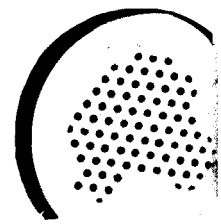

126 E

Incidental information

No. 17

Items of interest from our laboratory notebooks

9-(4-Dimethylaminophenyl)-2,3,7-trihydroxy-6-fluorone

A reagent for the spectrophotometric determination of **Ta** in the presence of **Zr, Nb** or **Ti.** (see V. A. Nazarenko and M. B. Shustova, *Zavodskaya Lab.* **2B,** 1283 (1957); C.A. **53,** 13874c (1959)). CODE 3862·3. Price 1g 9/9, 5g 40/-.

1,3-Diphenylpropan-1,3-dione (Dibenzoylmethane)

A reagent for the spectrophotometric determination of **U.** A procedure that includes ion-exchange separation from **Th** is described by H. J. Seim *et al. Anal. Chem.* **31,** 957 (1959). CODE 4004·45. Price 5g 7/6, 10g 13/6.

4-(2-Pyridylazo)-resorcinol, sodium salt (PAR)

An extremely sensitive reagent for the colorimetric determination of **Co, Pb** and **U.** (see F. H. Pollard *et al. Anal. Chim. Acta* **20,** 26 (1959)). CODE 7275·5. Price 1g 6/-, 5g 22/9, 10g 44/-.

o-(Hydroxymercuri)-benzoic acid

A titrimetric reagent for S^{2-}, **thiourea, xanthates, mercaptans** and many other organic sulphur compounds. (see M. Wronski *Analyst* **83,** 314 (1958)). CODE 4691. Price 1g, 12/6, 5g 52/6.

Phenyl 2-pyridyl-ketoxime

A colorimetric reagent for the determination of iron in strong alkalis and of **"oxidised" iron** in the presence of metallic iron. (see F. Trusell and H. Diehl *Anal. Chem.* **31,** 1978 (1959)). CODE 6711. Price 1g 30/-, 5g 135/-.

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